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**FAILURE MECHANISMS AND ACCELERATED LIFE TESTS
OF NICKEL-CADMIUM BATTERIES**

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and

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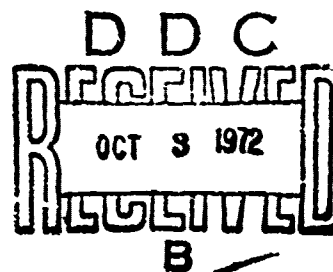
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13. ABSTRACT <p>Preliminary experiments indicated valid tests were developed with temperature gradients and/or with rates of discharge as the primary variables for accelerated life testing of sealed batteries. Depth of discharge was indicated to have only a very small effect on the life of cadmium electrodes. New sealed cells having longer life without, significant loss of performance, were designed and constructed. Verification tests were recommended for them.</p> <p>Supporting studies emphasized (a) the development of maintenance procedures for a battery testing laboratory, (b) the recommendation of approaches for empirical, statistical, and physical analysis of large amounts of battery life data, (c) the development of a physical basis for accelerated life tests based on springs, dash-pots, and their analogs as they relate to aging processes, (d) the measurement and calculation of thermal resistances and thermal capacitances of cells, components of cells, and combinations of cells in batteries, and (e) the amplification of a Battery Information Index</p>			

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FOREWORD

This report describes work performed during a three-year contract at the Columbus Laboratories of Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201, and at the Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio 45433. The work was done under Contract No. F 33615-69-C-1539, Task 314522-022. The report was submitted by the authors on June 30, 1972, and covers work done between May 1, 1969 and June 30, 1972.

This project was under the general direction and supervision of Dr. J. McCallum. Battelle personnel who have contributed to the various aspects of the work are:

Dr. E. W. Brooman - Accelerated Testing, Literature Review, and Failure Analysis

Mr. P. W. Cover - Increased Battery Life and Cell Fabrications

Mr. R. L. Gibbs - Facility Maintenance

Mrs. D. M. Johnson - Literature Review

Mr. O. L. Linebrink - Facility Maintenance

Dr. A. H. Reed - Accelerated Testing, Increased Battery Life, Cell Fabrication, Failure Analysis, and Literature Review

Mr. E. A. Roeger, Jr. - Accelerated Testing, Data Analysis, Facility Maintenance, Failure Analysis, and Literature Review

Dr. R. E. Thomas - Stress-Strain Models and Accelerated Testing

Dr. A. Fleischer, Consultant, 466 South Center Street, Orange, New Jersey 07050, has provided guidance in aspects of the program dealing with cell fabrication and failure analysis.

Mr. Gerald H. Miller, AFAPL/POE-1, is the cognizant Air Force Scientist. His efforts helped direct the work in two laboratories toward the needs of the U.S. Air Force.

Publication of this report does not constitute Air Force Approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

James D. Reams
Chief
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ABSTRACT

This report summarizes accomplishments during a three year work period on several tasks and subtasks as follows:

Task I. Accelerated Life Tests. Accelerated life tests for sealed cells were planned and given preliminary examination in the laboratory with 5 groups of 5 cells in each group. Specially prepared demountable cells having internal heaters were constructed with thin, commercially prepared nickel and cadmium electrodes. In one experiment, uniform temperatures of -20, -5, +10, +25, and +40 C were imposed and the effects of temperature on cell life was negligible. In a companion experiment having internal heaters at +40 C, the rates of degradation of cell qualities was accelerated about 10 times for each 30 degree temperature difference between inside and outside. In another experiment different discharge rates of C/2, C, 2C, 4C, and 8C were imposed with uniform cell temperatures of 25 C. A 10-times increase in discharge rate appeared to yield about a 30-times increase in the rate as which cell qualities degraded. In a companion experiment having internal heaters at +40 C, a 10-times increase in discharge rate appeared to yield about a 100-times increase in the quality-degradation rate. In another experiment with limiting cadmium electrodes, the effects of depth of charge were found to be much smaller than anticipated from published information. A factor of 10-times in the product of (depth of discharge x cycles) was required to yield an apparent degradation of capacities by a factor of only 2-times. A theoretical basis for accelerated life tests was refined and expanded by analogy with springs and dashpots. Ideal springs always store energy. Ideal dashpots always dissipate energy. This report correlates dashpot analogs though Onsager's reciprocal relations and correlates for the first time, spring analogs with the Tribus relations for thermostatics.

Task II. Improved Cells. Prototype nickel-cadmium cells were built with the following improvements: (1) thicker plaques, (2) thicker substrates, (3) moderate pore filling, (4) prolonged final washing of electrodes, (5) electrode matching, (6) polypropylene separator, (7) solid nickel terminals, combs, and tabs, and (8) "Mercury-cell"-grade potassium hydroxide. Comparative testing shows longer cell life with the incorporation of these improvements.

Task III. Supporting Studies. (a) Routines for maintaining a battery testing laboratory were worked out. (b) Procedures for analyzing large quantities of test data were recommended. (c) A physical and mathematical basis for combining

ABSTRACT (Continued)

springs, dashpots, inertial masses, and their analogs was developed. (d) Thermo-physical properties for the components of cells, and for batteries of cells were determined for resistance/capacitance networks and calculations were experimentally verified. (e) A battery information index having about 2200 documents was produced as a result of active engagements by the project personnel with the published technical literature throughout the course of the contractual program.

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FAILURE MECHANISMS AND ACCELERATED LIFE TESTS OF NICKEL-CADMIUM BATTERIES

J. McCallum and G. H. Miller

BACKGROUND AND OBJECTIVES

This final report summarizes a three-year program to develop concepts concerning accelerated testing of sealed spacecraft cells and batteries and to verify the concepts. The theoretical framework previously proposed^{(1,2,3)*} for both the United States Air Force and NASA shows that degradation of cell and battery performance should be controlled by applied stresses. Each stress is assumed linearly proportional to both the associated strains and to strain rates applied to the system. Furthermore, stresses were identified as intensity gradients for the degradation of various energy forms. The intensity gradients most pertinent to battery life and performance were identified as voltage gradients, temperature gradients, pressure gradients, and concentration gradients. This identification of stresses with gradients led to what was called the "gradient hypothesis", which says: All aging is caused by intensity gradients with their strains and strain rates. Therefore, the main objective of new work was to discover one or more accelerated test procedures. Also, efforts were planned to develop nickel-cadmium cells with longer life by designing the components so they would operate at stress levels lower than those found in present-day cells.

The work on this program was divided into the following three tasks:

- Task I. Accelerated Testing. The purpose of this task was to provide experimental evidence for the validity of selected tests and their theoretical basis.
- Task II. Increased Battery Life. The work of this task involved designing and developing nickel-cadmium cell components so the cells would operate at lower stress levels. This task complements Task I by using the same stress-strain and stress-strain rate phenomena for opposing purposes.

* References are listed on page 58.

Task III. Supporting Studies. This task was divided into five subtasks:

- (a) Facility Maintenance. This work involved maintaining the equipment in the Battery Laboratory of the Aero Propulsion Laboratory at Wright-Patterson Air Force Base in a state of readiness to perform the experimental portion of this program.
- (b) Data Analysis. Simulated orbital life tests begun under Contract No. AF 33(165)-3701 were continued under this contract. Cells that failed during these tests were analyzed for failure determinants and failure mechanisms.
- (c) Stress-Strain Models. A mathematical model based on springs and dashpots was developed to describe the aging of an energy storing device. An objective was to improve the theoretical basis for new accelerated test procedures and improved cells in Tasks I and II.
- (d) Thermophysical Properties. Thermophysical properties were determined for individual cell components so that improved models of heat flow in cells and batteries could be used to predict improved designs for cells and batteries.
- (e) Literature Review. A continuing review of literature in the field of nickel-cadmium battery technology and accelerated testing was performed to help keep project personnel up to date in the field.

Each of these tasks and subtasks is discussed in detail in subsequent sections of this report.

TASK I. ACCELERATED LIFE TESTS

A Physical Basis for Accelerated Life Tests

In previous work for the U. S. Air Force^(1,2) a theoretical basis for accelerated life tests was proposed. Development of fundamental concepts was continued for NASA.⁽³⁾ During this new contract period, fundamental concepts were refined and enlarged upon, as explained in sections to follow.

Table I, shows earlier relationships proposed for generalized stress-strain and stress-rate-of-strain involving eight forms of energy. For accelerated life testing of batteries, only four forms of energy were deemed to be germane, namely, (1) three dimensional mechanical energy in Row 3, (2) electrical energy in Row 4, (3) thermal energy in Row 5, and (4) chemical energy in Row 6. For each energy form, the primary cause of "aging" and shortened life was attributed to stresses. Stresses were associated with gradients of the intensity factors from Column 3, as given in Column 5 for the "Flux Generality" and in Column 7 for the "Stress-Strain Generality", namely gradients of pressure, voltage, temperature, and concentration. This prior work thereby led to aforementioned "gradient hypothesis".

One of the unusual aspects of this approach to accelerated life tests was an implication that temperature, itself, was not a stress whereas temperature gradient was a stress. This implication is unusual because of well established and well known associations of chemical reaction rates with temperature and because of allied associations of chemical reaction rates with "aging". To remain consistent with the gradient hypothesis, therefore it was supposed that an increase of temperature could create or change gradients of concentrations, voltages, and/or pressures. Thereby, the various kinds of intensity gradients should be associated with an absolute value of uniform temperatures. This sort of reasoning was in mind during the planning of the experimental program. Thus, the next section of this report describes two parts of an experiment in which variables were supposedly controlled identically except that in one part of the experiment cell temperatures were held uniform, in the other part, internal temperature gradients were imposed. Similarly, another experiment, described later under Rate of Discharge has two parts: one with internal temperature gradients and one without temperature gradients.

A third experiment described later under Depth of Discharge extended the testing of the gradient hypothesis, as follows. In the context of Table I, depth of discharge appears as an amount factor per unit in Column 7 of Row 4. Voltage

gradients were thereby implied to be the stress directly associated with the various levels of depth of discharge. At the same time, the earlier theoretical framework implied existence of gradients of pressure, temperature, or concentration somehow coupled with the voltage gradients. Voltage gradient, of course, are directly coupled to electrical charge per unit area, that is, the depth of discharge. Therefore, the Depth of Discharge Experiment was planned to provide physical evidence for how and to what extent these various stresses were related to each other and to the electrical strain called depth of discharge.

A fourth experiment was planned with varying concentrations of carbonate in the electrolyte. This experiment was devised because large carbonate concentrations had frequently been found to be associated with failure mechanisms.^(2,4) Moreover, concentration gradients show in Row 6 of Table I as one of the important stresses and an experiment designed to study this stress under controlled conditions seemed to be a very desirable experiment to perform. In the actual course of events, however, the Carbonate Experiment was abandoned when Barney and Catotti published their comprehensive findings on the "Effects of Carbonates on Charge and Discharge Characteristics of Sealed Nickel-Cadmium Cells".⁽⁵⁾ Therefore, the effects of carbonate received little direct study during this contractual period. Nevertheless, the above mentioned knowledge from Barney and Catotti⁽⁵⁾ as well as results from this project^(2,4) shows the effects of carbonate concentration to be consistent with the physical basis for structuring an accelerated life test. In the meantime, the physical concepts and relationships continued under development with the three tasks of this program.

In Subtask III(e) on "Stress-Strain Models", the fundamental concepts inherent in Table I continued to be refined and improved. First of all, the stress-strain model was related to mechanical springs and mechanical dashpots. An ideal spring is a mechanical device in which mechanical stress is proportional to mechanical strain. An ideal dashpot is a mechanical device in which stress is proportional to strain rate. Real examples of springs and dashpots are given by the springs and the shock absorbers on automobiles, respectively. The first six rows of energy forms in Table I were then related by analogy with ideal springs and ideal dashpots. The final results of these deliberations are given in Table XIII.

The spring and dashpot analogies were utilized for the purpose of emphasizing these most important points:

- Point (a). Ideal spring (and their analogs) always store energy and never dissipate energy, whereas
- Point (b). Ideal dashpots (and their analogs) always dissipate energy and never store energy.⁽⁶⁾

TABLE I. GENERALIZED STRESS-STRAIN AND STRESS-RATE-OF-STRAIN RELATIONSHIPS

(1) Energy Form	(2) Energy Source	(3) Intensity Factor, I	(4) Amount Factor, A	(5) Flux Generality $\frac{1}{A} \frac{\partial A}{\partial t} = k_8 \frac{\partial I}{\partial x}$ (a)	(6) Conservation Generality $\frac{\partial I}{\partial t} = k_{17} \frac{\partial^2 I}{\partial x^2}$	(7) Stress/Strain Generality $\frac{\partial I}{\partial x} = k_{27} \frac{\partial A}{\partial t}$ (b)	(8) Impulse/Amount Generality $\Delta I = k_{33} \frac{\partial A}{\partial t}$	(9) Impulse/Rate Generality (c) $\Delta I = k_{44} \frac{\partial^2 A}{\partial t^2}$
1. Mechanical (one de- gree of freedom)	Motion	Force, F	Distance, x	Not appropriate	Not appropriate	Not appropriate	$\Delta F = k_{34} \frac{\partial x}{\partial t}$ (Newton's 1st Law, Stoke's Law)	$\Delta F = k_{46} \frac{\partial^2 x}{\partial t^2}$ (Newton's 2nd Law)
2. Mechanical (two de- grees of freedom)	Liquids	Surface tension, γ	Area, a	Not appropriate	Not appropriate	Not appropriate	$\Delta \gamma = k_{36} \frac{\partial a}{\partial t}$	$\Delta \gamma = k_{44} \frac{\partial^2 a}{\partial t^2}$
3. Mechanical (three de- grees of freedom)	Liquids or gases	Pressure, P	Volume, V	$\frac{1}{A} \frac{\partial V}{\partial t} = k_{11} \frac{\partial P}{\partial x}$ (Poiseuille's Law)	$\frac{\partial P}{\partial t} = k_{18} \frac{\partial^2 P}{\partial x^2}$	$\frac{\partial P}{\partial x} = k_{29} \frac{\partial V}{\partial t}$ (Sound energy)	$\Delta P = k_{37} \frac{\partial V}{\partial t}$ (Poiseuille's Law)	$\Delta P = k_{44} \frac{\partial^2 V}{\partial t^2}$
4. Electrical	Elec- tricity	Voltage, E	Charge, Q	$\frac{1}{A} \frac{\partial Q}{\partial t} = k_{14} \frac{\partial E}{\partial x}$ (Ohm's Law)	$\frac{\partial E}{\partial t} = k_{19} \frac{\partial^2 E}{\partial x^2}$ (Ohm's Law)	$\frac{\partial E}{\partial x} = k_{28} \frac{\partial Q}{\partial t}$ (Capacitance relationship)	$\Delta E = k_{38} \frac{\partial Q}{\partial t}$ (Ohm's Law)	$\Delta E = k_{47} \frac{\partial^2 Q}{\partial t^2}$ (Inductance relationship)
5. Thermal	Heat	Tempera- ture, T	Heat, q (calories)	$\frac{1}{A} \frac{\partial q}{\partial t} = k_{15} \frac{\partial T}{\partial x}$ (Fourier's Law)	$\frac{\partial T}{\partial t} = k_{20} \frac{\partial^2 T}{\partial x^2}$ (Fourier's Law)	$\frac{\partial T}{\partial x} = k_{27} \frac{\partial q}{\partial t}$	$\Delta T = k_{39} \frac{\partial q}{\partial t}$ (Fourier's Law)	$\Delta T = k_{44} \frac{\partial^2 q}{\partial t^2}$
6. Chemical	Chemical species in solution	Concentra- tion, C	Moles, M	$\frac{1}{A} \frac{\partial M}{\partial t} = k_{16} \frac{\partial C}{\partial x}$ (Fick's 1st Law)	$\frac{\partial C}{\partial t} = k_{21} \frac{\partial^2 C}{\partial x^2}$ (Fick's 2nd Law)	$\frac{\partial C}{\partial x} = k_{30} \frac{\partial M}{\partial t}$	$\Delta C = k_{40} \frac{\partial M}{\partial t}$ (Mass Action Law)	$\Delta C = k_{44} \frac{\partial^2 M}{\partial t^2}$
7. Kinetic	Motion	Velocity, v	Momentum, mv	$\frac{1}{A} \frac{\partial (mv)}{\partial t} = k_{22} \frac{\partial v}{\partial x}$ (Bernoulli's Theorem)	$\frac{\partial v}{\partial t} = k_{24} \frac{\partial^2 v}{\partial x^2}$	$\frac{\partial v}{\partial x} = k_{27} \frac{\partial (mv)}{\partial t}$	$\Delta v = k_{41} \frac{\partial (mv)}{\partial t}$ (Newton's 1st Law, Stoke's Law)	$\Delta v = k_{44} \frac{\partial^2 (mv)}{\partial t^2}$ (Hooke's Law)
8. Light	Radiation	Frequency, f	Illumina- tion, L (no. of photons)	$\frac{1}{A} \frac{\partial L}{\partial x} = k_{25} \frac{\partial f}{\partial x}$ (The Rad)	$\frac{\partial L}{\partial x} = k_{17} \frac{\partial^2 L}{\partial x^2}$	$\frac{\partial f}{\partial x} = k_{27} \frac{\partial L}{\partial t}$	$\Delta f = k_{42} \frac{\partial L}{\partial t}$ (Planck's Law)	Not appropriate

(a) Strain rate = k · stress.

(b) Stress = k · strain

(c) Force = k · acceleration.

Real springs and dashpots are never ideal and behave as though there were mixtures of springs and dashpots in real devices. Fortunately, the rules are well worked out for combining springs in series or in parallel with other springs or with dashpots. Fortunately too, mathematical descriptions of thermal and electrical analogs of mechanical springs, dashpots, and inertial masses are also well worked out. Unfortunately, however, some of the basic definitions for electrical and thermal components are inverted from analogous definitions for mechanical components. The inversions are unfortunate because they sometimes cause similar physical situations to be described differently. For example, electrical voltages in series are additive and voltages in parallel are the same on each device whereas mechanical forces in series are the same on each device and forces in parallel are additive. Even so, forces are analogous with voltages in several ways and a physical basis for accelerated life tests depends on the proper understanding and use of "forces", "displacements", "stresses", "strains", "strain-rates", and their analogs.

During the new contract period, considerable thought was given to refinements and improvements in the general concepts inherent in Table I. Noteworthy accomplishments are as follows with reference to Table I:

- Generalized forces are intensity factors in Column 3.
- Generalized displacements are amount factors in Column 4.
- The mathematical product of force times displacement should give appropriate units of work. Heat energy in Row 5 is an exception to this generalization. Therefore, suggestions have been made⁽⁷⁾ that intensity and amount factors for heat energy should be sought and developed such that (a) their mathematical product gives units of thermal work and (b) the new intensity factor has all the properties of temperature. A dimension of velocity is suggested as the appropriate new unit to be developed as the appropriate intensity factor for thermal energy. Then, heat would be treated as kinetic energy with an amount factor of momentum in accordance with Row 7.
- Generalized stresses and strains differ from generalized forces and displacements by the geometry of the components under consideration. Thus, the mathematical product of stress times strain should give appropriate units of work/volume, whereas force times displacement gives work.

- There are two kinds of stresses. They have different units. They can interact with one another through common units yet they are conceptually quite different. The first kind of stress appears as analogs of springs for the storage of energy, wherein stress is proportional to strain. The second kind of stress appears as analogs of dashpots for the dissipation of energy, wherein stress is proportional to strain rate. The spring analog of thermal stress is temperature; the dashpot analog of thermal stress is temperature gradient. Similarly, the spring analog of chemical stress is concentration and the dashpot analog of a chemical stress is a concentration gradient. At the same time these distinctions are noted about stresses, the associated distinctions about strains and strain-rates must be noted also. The spring analog of strain will have units of amounts/volume. The dashpot analogs of strain rates will describe fluxes having units of amounts/(area·time). Then, the spring analogs of stress times strain always give units of work/volume. The dashpot analogs of stress times strain-rate always give units of power/volume = work/(volume·time).
- The various dashpot analogs in Column 5 are related to each other through Onsager's reciprocal relations.⁽⁸⁾ Onsager's relations state that any given flux on the left-hand side of the equations in Column 5 is equal to the sum of the contributions to that flux caused by all the intensity gradients on the right-hand side of the equation in Column 5. Readers may note, of course, that forms of energy exist which are not in Table I and, therefore Onsager's relations are not limited to information in Column 5. However, since the important forms of energies in batteries have been judged to be limited to mechanical, electrical, thermal, and chemical, let us use the letters Me, E, T, and C as subscripts to denote these respective energy forms from Rows 3 through 6. Then, using the intensity factors and amount factors from Columns 3 and 4 with their respective symbols, the Onsager relations state as follows:

$$(1/a)(\partial V/\partial t) = k_{MeMe} \cdot \partial P/\partial x + k_{MeE} \cdot \partial E/\partial x + k_{MeT} \cdot \partial T/\partial x + k_{MeC} \cdot \partial C/\partial x \quad (1)$$

$$(1/a)(\partial Q/\partial t) = k_{EMe} \cdot \partial P/\partial x + k_{EE} \cdot \partial E/\partial x + k_{ET} \cdot \partial T/\partial x + k_{EC} \cdot \partial C/\partial x \quad (2)$$

$$(1/a)(\partial q/\partial t) = k_{TMe} \cdot \partial P/\partial x + k_{TE} \cdot \partial E/\partial x + k_{TT} \cdot \partial T/\partial x + k_{TC} \cdot \partial C/\partial x \quad (3)$$

$$(1/a)(\partial M/\partial t) = k_{CMe} \cdot \partial P/\partial x + k_{CE} \cdot \partial E/\partial x + k_{CT} \cdot \partial T/\partial x + k_{CC} \cdot \partial C/\partial x \quad (4)$$

To read these equations consider the second, the electrical flux relation, which might be read as follows:

"The amount of electrical charge, ∂Q , per unit area, a , per unit of time, ∂t , is called 'an electrical flux' and the total flux is equal to the sum of the electrical flux caused by a pressure gradient plus the electrical flux caused by a voltage gradient plus the electrical flux caused by a temperature gradient plus the electrical flux caused by a concentration gradient."

The other equations above can be read similarly. Obviously, the major portion of each flux will be associated with its directly related gradient in Rows 3 through 6. But any portion of flux occurring as a result of coupling with the other gradients also contributes to the dissipation of energy in the device. The above Onsager relations in appropriate combinations are a vital part of a physical basis for accelerated life tests,

- Another vital part of a physical basis for accelerated life tests is indicated by the Tribus relationships.⁽¹⁷⁾ These relationships utilize analogs of spring wherein the stress units are intensity factors in Column 3 and strain units are amount/volume. Using, then, the amount factors in Column 4 with brackets to denote the respective amounts/volume, the Tribus relations state as follows:

$$\partial[V]/\partial x = k'_{MeMe} \cdot \partial P/\partial x + k'_{MeE} \cdot \partial E/\partial x + k'_{MeT} \cdot \partial T/\partial x + k'_{MeC} \cdot \partial C/\partial x \quad (5)$$

$$\partial[Q]/\partial x = k'_{EMe} \cdot \partial P/\partial x + k'_{EE} \cdot \partial E/\partial x + k'_{ET} \cdot \partial T/\partial x + k'_{EC} \cdot \partial C/\partial x \quad (6)$$

$$\partial[q]/\partial x = k'_{TMe} \cdot \partial P/\partial x + k'_{TE} \cdot \partial E/\partial x + k'_{TT} \cdot \partial T/\partial x + k'_{TC} \cdot \partial C/\partial x \quad (7)$$

$$\partial[M]/\partial x = k'_{CMe} \cdot \partial P/\partial x + k'_{CE} \cdot \partial E/\partial x + k'_{CT} \cdot \partial T/\partial x + k'_{CC} \cdot \partial C/\partial x \quad (8)$$

In the above equations the ∂x values cancel out of all terms. When the ∂x term is deleted, the result is a direct stress-strain relationship such that strains are amounts/volume and stresses are intensities and stress times strain has units of work/volume.

- The coefficients in both the Onsager and in the Tribus relationships are called "reciprocal" relations because cross coefficients with the same subscript symbols are numerically equal. For example, k_{MeE} in the first Onsager relation Equation (1) above is equal to k_{EMe} in Equation (2). Likewise, k'_{MeE} in the first Tribus relation Equation (5) is equal to k'_{EMe} in Equation (6).
- Insofar as the degradation of qualities is brought about by the physical movement or rearrangement of physical matter, only interactions of stresses and fluxes involving matter cause aging. This means k_{EE} , k_{ET} , k_{TE} , k_{TT} , $(1/a)(\partial Q/\partial t)$, and $(1/a)(\partial q/\partial t)$ are not directly associated with failure mechanisms. All other terms and couplings in the Onsager relations are.
- All the Onsager and Tribus relations behave as a simple Maxwell element of springs and dashpots in a series. Therefore, the time to failure is given by an Equation of the type:

$$t_f = (b/k) \ln[x(o)/(L-L_F)] \quad (9)$$

Here, L_F is the predefined failure extension of the Maxwell element.

L is the experimental constant extension at which the device is held from time t_o to time t_f .

$x(o)$ is the difference between the equilibrium extension of the device at time t_o and extension L .

b is the combined dashpot constant.

k is the combined spring constant.

Because $x(o)$, L , and L_F will be fixed for any given test condition, it is seen that the time to failure depends primarily on the ratio of the dashpot constant to the spring constant, b/k .

- For a valid accelerated life test the above ratio of constants, b/k , must be made to decrease with increasing stress levels. If values of b/k can be determined to be a function of some experimentally

controlled variable z such that $b/k = f(z)$, this relation may then be used to obtain an extrapolated time to failure at a "normal" condition of stress levels.

The above conclusions and accomplishments with regard to a physical basis for accelerated life tests require further quantitative development. However, the general Onsager and Tribus relationships in combination appear to provide a sufficient basis for describing accelerated life tests. Further work is needed to authenticate the general validity of these relationships.

Temperature and Temperature Gradients

Details of the two experiments summarized below are given in a special report titled, "Temperature and Temperature Gradients for Accelerated Life Tests of Nickel-Cadmium Cells".⁽⁹⁾ Briefly summarized, cycling tests were performed on groups of five cells each at ambient temperatures of -20, -5, 10, 25, and 40 C and both with and without temperature gradients. Special demountable cells with internal heaters were made and used to provide an internal cell temperature of 40 C for those cells with temperature gradients.

In all these cells, the failure determinant was a loss of capacity at the positive electrode. Actually, both positive and negative electrodes lost substantial ampere-hour capacity during the tests and the negative electrodes lost the most. However, failures to discharge within test specification times were caused by inadequate capacities at the positive electrodes and so failure determinants were associated with the positives.

All cells in these experiments were made with thin, commercial electrodes from special aircraft batteries. As part of the failure analysis, these electrodes were found to contain substantial quantities of soluble nitrate impurities. A strong odor of ammonia emanated from all demountable cells after the tests. As a result of these and other findings during failure analysis, the failure mechanism was associated with a "nitrate-nitrite shuttle" which acted like a partial internal electrical short. The same mechanism appeared to control all failures and degradations of qualities. Because the failure mechanism appeared to be the same for all cells, the accelerated life test was deemed to be a valid life test.

In these experiments, the effect of a constant temperature level on degradation of cell qualities appeared to be negligible. On the other hand, cells with maximum temperature gradients gave an acceleration factor of about 35 compared

with cells in the same tests but with no temperature gradient. Thus, in the five tests at +40, +25, +10, -5, and -20 C both inside and outside the cells, the rate of change of voltage qualities per cycle was practically the same for all cells. On the other hand, with the five tests having the same five external temperatures but with all cells having the same internal temperature of +40 C for all tests, the acceleration factors appeared to increase about 10 times for each 30-degree differential between internal and external temperatures. Both tests had large and mostly unexplained differences between cells but the statistics suggest that the above conclusions are correct with at least a 70 percent probability.

Cell temperatures varying between +40 and -20 C were expected to show significant differences in the rates at which cells failed. The fact that no such effect was observed is attributed to the particular failure mechanism, namely the "nitrate shuttle". Thus, it is supposed that the concentration of the very soluble nitrates was unaffected by the absolute level of temperature. The rate of the nitrate-nitrite reactions with active electrode materials also appeared to be unaffected by the absolute temperature level. The net result was an absence of any observable effect of temperature level on cell life. On the other hand, the effect of temperature gradients was to bring about nonuniform gradients of all kinds within cells as explained in the next section of this report.

From the viewpoints of a physical basis for accelerated life tests described in the preceding section, temperature and temperature gradients are possibly important any time temperature appears in the Onsager or in the Tribus relationships. Thus, from the previously written Onsager relations, temperature gradients can cause:

- (a) Volumes to move by convection or by osmosis
- (b) Charge to move by the Soret effect or by concentration gradients
- (c) Chemicals to move by convection or by concentration gradients.

The absolute temperature itself can increase or decrease:

- (a) Volume by expansions or by contractions
- (b) Electrical charge through ionizations or by changing solubilities
- (c) Chemical concentration by changing solubilities or by changing chemical reaction rates as expected from the Arrhenius equation. (7)

In the above particular experiments, it appears that convection and concentration gradients may have been responsible for the accelerations found with temperature gradients but not with uniform temperatures.

In future experiments involving temperature gradients it is recommended that heaters be placed outside rather than inside, as was done with these experiments. Thereby, the variations between cells in the same tests would be expected to be much more closely controlled.

Rate of Discharge

Details of the two experiments summarized below are given in a special report titled, "Rate of Discharge for Accelerated Life Tests of Nickel-Cadmium Cells".⁽¹⁰⁾ Briefly summarized, cycling tests were performed on groups of five cells each discharged to 50 percent depth and at C/2, C, 2C, 4C, and 8C rates. Environmental temperature was 25 C for both experiments but one experiment of five groups had specially constructed internal heaters maintained at +40 C.

The failure determinant and failure mechanism for these cells were found to be the same as those described in the previous section, namely, an excessive loss of capacity at positive electrodes caused by the "nitrate-nitrite shuttle".

The effect of temperature gradients with these two experiments confirmed the effects mentioned in the previous section, namely, a temperature difference of about 30 degrees between heaters inside and environmental temperature outside appeared to give about a 10 times increase in acceleration factors compared with similar cells having uniform temperature. In these rate of discharge experiments, however, the effect of temperature gradient on an acceleration factor appears to be favored with about a 95 percent probability compared to a 70 percent probability in the previous two temperature experiments.

The effect of rate of discharge was relatively large. Thus, acceleration factors increased about 30 times for each 10-times increase in discharge rates. Unfortunately, the observed differences were also large between cells in the same group and, because of these large variations, confidence in the above conclusion is not as high as it should be for a widely accepted accelerated life test. The probability is at least 70 percent in favor of rate of discharge as a useful strain-rate for accelerating the life tests of batteries.

The acceleration factors for temperature gradients combined with acceleration factors from rates of discharge give about a 100-times increase

in acceleration factors for each 10-times increase in rate of discharge. These important findings imply that future life tests with nickel-cadmium batteries might be accelerated two ways. First, by discharging 10-times faster and with an imposed temperature gradient, a cell could be made to degrade in quality perceptibly with, perhaps 1 percent of the normal number of cycles to the same level of degradation. Second, if discharge rates are increased 10-times, it follows that the duration of each cycle could be shortened. The combination of discharge rates with temperature gradients, therefore might shorten the duration of an accelerated life test as much as 1000 times.

From the viewpoints of a physical basis for accelerated life tests, rate of discharge is possibly important whenever rate of discharge can be associated with one of the parallel stresses in the Onsager and Tribus relations. The main effect to be associated with rates of discharge would be expected to be voltage gradients. This expectation follows because variation in rate of discharge for any given cell design becomes a current density variable. However, concentration gradients associated with current densities may be more important, insofar as the physical movement and rearrangement of matter is concerned. Thereby, concentration gradients become directly coupled with current densities. In addition, the relationship between current densities and temperature becomes more pronounced with increasing current densities because Joule heating is proportionate to the square of the current. With Joule heating, nonuniformities of temperature are to be expected. With nonuniformities, aging effects can be expected to accumulate faster as smaller areas are "attacked" separately.

In this particular experiment, the main effect of increasing current densities appears to have been the associated increased concentration gradients which, in turn, enhanced the adverse effect of the "nitrate-nitrite shuttle".

Depth of Discharge

Details of this experiment are given in a special report titled, "Depths of Discharge for Accelerated Life Tests of Cadmium Electrodes."⁽¹¹⁾ Briefly summarized, cycling tests were performed with thin cadmium electrodes taken from the same commercial cells as used to build demountable cells for the previously mentioned experiments. Portions of the commercial cadmium electrodes were cut to 1-1/2 by 3 inches and placed between two pieces of nickel-oxide electrodes, 2-3/4 by 5-1/2 inches. The electrodes were wrapped with perforated polypropylene separators, placed in special Lucite cells, and flooded with KOH electrolyte. After careful matching of electrodes for similar electrical performances

and for state of charge, five cells were placed in each group and the five test groups were cycled as follows:

<u>Additional Depth of Discharge Beyond an Initial 10 percent</u>	<u>Discharge Time, minutes</u>	<u>Charge Time, minutes</u>
10	6	12
20	12	24
40	24	48
60	36	72
80	48	96

One electrode was removed, from each test group for characterization and analysis after 100, 200, 400, 800, and 1600 cycles. Otherwise, all cells and groups were supposedly identical in content and in experimental conditions.

The net result of this fairly sophisticated experiment was that depth of discharge has a relatively small effect on the quality of cadmium electrodes. There definitely was a decrease in utilizable cadmium in those electrodes having the combinations of large depth of discharge with large number of cycles. A factor of about 10 times in this product of (depth of discharge)·(number of cycles) was required to observe a 2 times decrease in available capacity. Very little cadmium was observed to migrate out of the electrodes. The relatively small losses of capacity were attributed to a change in structure of the charged cadmium. The charged cadmium may also have become buried or hidden in pores with the extensive cycling so that it became electrically isolated and could not be oxidized. Evidence for this latter mechanism is indicated by a series of photomicrographs and chemical analyses for portions of electrodes going through these depth of discharge tests.⁽¹¹⁾

From a practical point of view, the use of depth of discharge to arrive at a valid accelerated life test was anticipated because of widespread information in the literature which makes, or implies, such claims. Francis reviews some of the relevant information.⁽¹²⁾ If depth of discharge does, in fact, accelerate the failure rate of sealed nickel-cadmium cells, such an effect must be associated with the positive electrodes or with other variables not studied in this experiment.

From the viewpoint of the previously described physical basis for an accelerated test, there is no reason to expect that depth of discharge, itself, would have anything directly to do with aging mechanism. This reasoning follows because depth of discharge is analogous with releasing some of the displacement

on a spring. So long as the spring, or its analog is an ideal spring, energy would either be stored or be given back from storage and only the associated dashpot components would contribute to irreversibility of the processes. Future work will be required to identify the dashpot analogs that should be associated with depth of discharge. Even more work will be required to identify experimental conditions where the dashpot components can be measured and where the dashpot coefficient, "b", will have a significant effect on the time-to-failure, t_f in the previously itemized failure Equation (9).

Verification Tests

Contractually, the verification tests were designed to "include normal (real-time) and accelerated tests in order to verify that the failure rates and mechanisms of the accelerated tests correspond to those experienced in the real-time testing". The verification tests were set up with commercial cells to confirm evidence described previously in preliminary tests using specially demountable cells. Two new tests were proposed, (1) a charge strain-rate test using 20 ampere-hour sealed cells and (2) a discharge strain-rate test using 6 ampere-hour sealed cells.

Test Design

Charge Strain-Rate Test. This test consists of five groups of six cells each. The test parameters are listed in Table II. Each group is charged at different Step 1 rates of charge to a voltage limit, at which time the charge is switched to the Step 2 rate of charge. Although the charge rate switchover is caused by a voltage controller on the group voltage, the switchover is set up on the first cycle so that it occurs exactly when the cells become 100 percent recharged. The voltage of the group at 100 percent recharge on the first cycle is then used for the switchover voltage during charge for the remainder of the life tests. The Step 1 and Step 2 charge times add to a total 3-hour charge period. This procedure was used because of the impurities found in these cells (described later in the report).

The discharge portion of each cycle is 7.5 amperes for 1 hour so that the lowest charge rate is able to replace the discharged capacity with a minimum overcharge of 13 percent.

TABLE II. VERIFICATION TEST PLAN

Group No.	<u>Charge Current</u>		High Charge Time, min	Discharge Current amp	Discharge Time, min
	Step 1, amp	Step 2, amp			
<u>Charge Strain-Rate Test (20 amp-hr Cells)</u>					
C-1	48.0	2.0	9.4	7.5	60.0
C-2	24.0	2.0	18.8	7.5	60.0
C-3	12.0	2.0	37.5	7.5	60.0
C-4	6.0	2.0	75.0	7.5	60.0
C-5	3.0	2.0	150.0	7.5	60.0
<u>Discharge Strain-Rate Test (6 amp-hr Cells)</u>					
D-1	3.0	0.6	60.0	3.0	60.0
D-2	3.0	0.6	60.0	6.0	30.0
D-3	3.0	0.6	60.0	12.0	15.0
D-4	3.0	0.6	60.0	24.0	7.5
D-5	3.0	0.6	60.0	48.0	3.8

Selected cells are to be removed from each group for parametric failure during the life of the group. One cell will be removed when its quality has degraded one-third of the difference between its initial and failure qualities. A second cell will be removed when its quality has degraded by two-thirds. In this manner, analysis can be performed on two parametric failures and still leave four cells to complete the test. Any cell's quality which fails below its failure quality will be removed immediately from test for failure analysis.

Discharge Strain-Rate Test. This test consists of five groups of six cells each. The test parameters are also listed in Table II. Each group is charged at the Step 1 rate of charge (3.0 amperes) for 60 minutes and then switched to the Step 2 rate of charge (0.6 ampere) for the remainder of the 3-hour charge period. Although the charge rate switchover is caused by a voltage controller on the group voltage, the switchover is set up on the first cycle so that it occurs exactly after the cells have been charged at the Step 1 rate for 1 hour. The cells are then subjected to 2 hours at the Step 2 rate of charge. This procedure was used because of the impurities found in the cells, as explained in the section on Cell Descriptions.

Each group is discharged to 50 percent of its rated capacity (6 ampere-hours). The discharge rates for the various groups are given in Table II. Those groups which require less than 1 hour for their discharge remain on open circuit for the remainder of the 1-hour discharge period.

Two cells in each of these groups are to be removed for parametric failures. These cells are to be removed in the same manner as explained for the cells removed in the Charge Strain-Rate Test.

Cell Descriptions

As previously explained, the Charge Strain-Rate Test uses commercial 20 ampere-hour cells while the Discharge Strain-Rate Test uses commercial 6 ampere-hour cells. These cells had been purchased under a previous contract (Contract AF 33(615)3701) and had been stored shorted for over 3 years before being used.

Because of the difficulties associated with the amount of carbonate and nitrate found in cells from previous experiments^(9,10), one 6 ampere-hour and one 20 ampere-hour cell were subjected to a chemical analysis for carbonate and nitrate. Samples of positive electrodes, negative electrodes, and separators from

each cell were analyzed. The results of these analyses were used to calculate the total weight of nitrate and carbonate in the cells as KNO_3 and K_2CO_3 . The quantities of carbonate and nitrate found in the commercial cells are listed in Table III.

TABLE III. QUANTITIES OF KNO_3 AND K_2CO_3 IN COMMERCIAL CELLS

Cell	Total Weight KNO_3 , mg	Total Weight K_2CO_3 , g
20 amp-hr	93	24.1
6 amp-hr	24	7.4

The quantities of impurities in the two cells are in about the same ratio as their rated capacities and appear to be high enough that they could be detrimental to the cells operation. Since no other cells were available, these commercial cells were still used for the verification tests. Because of relatively large concentrations of carbonate and nitrate, recommendations were made that the effect of carbonate on charging voltages be taken into account by emphasizing matching of cells at end of charge and by appropriate consideration of "charged qualities" in terms of initially measured values.

Cell Characterization and Matching

In order to characterize and obtain the data required to match the cells, both the 6 ampere-hour and 20 ampere-hour cells were subjected to the following steps:

- (1) Weigh cells and visually inspect for leaks.
- (2) Charge at $C/20$ for 48 hours with 1.50-volt limit.
(C = manufacturer's rated capacity)
- (3) Discharge at $C/3$ to 1.0 volt.
- (4) Short with 1-ohm resistors for 16 hours then dead short for 1 hour.
- (5) Charge at $C/10$ for 24 hours - record voltage.
- (6) Discharge at $C/2$ to 1.0 volts - record voltage and time.

- (7) Short with 1-ohm resistors for 16 hours then dead short for 1 hour.
- (8) Charge at C/10 for 24 hours - record voltage and measure internal resistance.
- (9) Discharge at C/2 to 1.0 volts - measure internal resistance and calculate capacities to 1.1 volts and 1.0 volt.

The results of these characterization and capacity determination steps are given in Tables IV and V.

The cells were matched into groups using their capacities determined in Step (9) and their internal resistances and charge voltages obtained in Step 8.

Test Apparatus

Once matched into six-cell groups, the cells were mounted in environmental chambers on Plexiglas base plates. A thermocouple was placed on one side of the cell in the approximate electrode center between the cell case and the retaining plate. The cells were then wired in series to a charge-discharge cycling rack to provide automatic testing. Figure 1 shows a circuit diagram of this test apparatus. The apparatus requires testing the cells as a group with no facilities for automatically disconnecting a cell if its voltage falls below acceptable levels. A group safety feature is provided such that the group will be open circuited if the group voltage falls below a preset limit.

The individual cell discharge voltages, individual cell temperatures, group voltages and group currents are recorded on 24-point recorders. The voltage recorders have been modified so that data are recorded only during the last 40 to 45 seconds of each discharge. During this recording period, the speed of the recorders is such that one of the 24 recorder points is measured and recorded every 1.67 seconds. Thus, it takes 40 seconds to read all 24 recorder points.

Data Analysis

Because of the data problems previously discussed,⁽⁹⁾ a simplified method of data handling was devised for the verification tests. As explained in the previous section, individual cell data are recorded only during the last 40 seconds of each discharge cycle. This data, along with the discharge current

TABLE IV. CHARACTERIZATION, CAPACITY, AND FAILURE DETERMINATION DATA FOR CHARGE STRAIN-RATE TEST

Group No.	Cell No.	Cell Weight, grams	End of Charge, volts	Internal Resistance, $\Omega \times 10^{-3}$	Capacity, ampere-hours		n, hours	g, g/amp-hr	IR $\times 10^{-2}$	ngIR	Failure	
					To 1.1 v	To 1.0 v					Volt, volt	Quality, amp/gram
C-1	750	886.4	1.47	2.99	26.7	27.2	2.667	44.32	2.24	2.65	0.978	0.378
	752	890.3	1.48	2.96	26.7	27.3	"	44.52	2.22	2.64	0.978	0.379
	759	888.1	1.47	2.90	26.5	26.8	"	44.41	2.18	2.58	0.978	0.388
	761	892.6	1.46	2.85	26.5	26.8	"	44.63	2.14	2.55	0.979	0.392
	764	888.8	1.48	2.87	26.5	27.2	"	44.44	2.15	2.55	0.978	0.392
	772	885.2	1.47	2.65	26.5	26.8	"	44.26	1.99	2.35	0.980	0.425
C-1	753	886.9	1.47	2.96	26.7	26.8	2.667	44.35	2.22	2.63	0.978	0.380
	755	894.5	1.47	2.93	26.7	27.0	"	44.73	2.20	2.62	0.978	0.382
	756	885.6	1.47	2.89	26.7	27.0	"	44.28	2.17	2.56	0.978	0.391
	760	887.0	1.47	2.88	26.8	27.2	"	44.35	2.16	2.55	0.978	0.391
	763	891.3	1.47	2.84	26.7	27.2	"	44.57	2.13	2.53	0.979	0.395
	771	886.5	1.47	2.75	26.7	27.2	"	44.33	2.06	2.44	0.979	0.410
C-3	743	887.0	1.47	2.98	26.3	27.0	2.667	44.35	2.24	2.65	0.978	0.378
	749	884.6	1.47	2.98	26.3	27.0	"	44.23	2.24	2.64	0.978	0.379
	754	887.9	1.47	2.90	26.5	27.0	"	44.40	2.18	2.58	0.978	0.388
	765	887.3	1.47	2.88	26.3	26.7	"	44.37	2.16	2.56	0.978	0.391
	769	882.8	1.48	2.70	26.2	26.7	"	44.14	2.03	2.39	0.980	0.419
	773	887.3	1.47	2.85	26.2	26.8	"	44.37	2.14	2.53	0.979	0.395
C-4	751	891.1	1.47	2.89	27.0	27.2	2.667	44.56	2.17	2.58	0.978	0.388
	762	889.7	1.47	2.93	27.2	27.5	"	44.49	2.24	2.66	0.978	0.376
	768	885.0	1.48	2.64	27.0	27.7	"	44.25	1.98	2.34	0.980	0.427
	770	890.1	1.47	2.82	26.8	27.3	"	44.51	2.12	2.52	0.979	0.397
	774	888.2	1.49	2.78	27.2	27.7	"	44.41	2.09	2.48	0.979	0.403
	775	885.8	1.48	2.75	27.0	27.3	"	44.29	2.06	2.43	0.979	0.411
C-5	744	887.5	1.48	3.03	26.2	27.0	2.667	44.38	2.27	2.69	0.977	0.372
	745	887.7	1.47	3.01	25.7	26.3	"	44.39	2.26	2.68	0.977	0.373
	747	888.8	1.49	2.98	25.5	26.0	"	44.44	2.24	2.65	0.978	0.378
	757	884.4	1.47	2.88	25.7	26.2	"	44.22	2.16	2.55	0.978	0.392
	758	883.9	1.47	2.89	26.2	26.5	"	44.20	2.17	2.56	0.978	0.391
	767	893.1	1.48	2.84	25.5	26.5	"	44.66	2.13	2.54	0.979	0.394

TABLE V. CHARACTERIZATION, CAPACITY, AND FAILURE DETERMINATION DATA FOR DISCHARGE STRAIN-RATE TEST

Group No.	Cell No.	Cell Weight, grams	End of Charge, volts	Internal Resistance, $\Omega \times 10^{-3}$	Capacity, ampere-hours		n, hours	g, g/amp-hr	IR $\times 10^{-2}$	ngIR	Failure	
					To 1.1 v	To 1.0 v					Volt, volt	Quality, amp/gram
D-1	362	271.1	1.48	3.1	7.30	7.35	2.0	45.18	0.93	0.34	0.901	1.19
	364	271.1	1.48	3.1	7.30	7.40	"	45.18	0.93	0.84	0.991	1.19
	378	271.5	1.48	2.9	7.30	7.35	"	45.25	0.87	0.79	0.991	1.27
	380	269.7	1.48	2.8	7.30	7.35	"	44.95	0.84	0.76	0.992	1.32
	381	272.2	1.48	2.9	7.30	7.40	"	45.37	0.87	0.79	0.991	1.27
	382	268.8	1.48	2.8	7.25	7.40	"	44.80	0.84	0.75	0.992	1.33
D-2	356	272.7	1.48	3.2	7.15	7.25	1.0	45.45	1.92	0.87	0.981	1.15
	359	272.3	1.48	3.2	7.20	7.25	"	45.38	1.92	0.87	0.981	1.15
	361	270.8	1.48	3.1	7.20	7.35	"	45.13	1.86	0.84	0.981	1.19
	365	269.5	1.47	3.0	7.20	7.30	"	44.92	1.80	0.81	0.982	1.23
	366	271.0	1.47	3.1	7.25	7.30	"	45.17	1.86	0.84	0.981	1.19
	376	272.8	1.49	3.0	7.25	7.40	"	45.17	1.80	0.82	0.982	1.22
D-3	362	270.5	1.48	3.1	7.40	7.50	0.5	45.08	3.72	0.84	0.963	1.19
	367	270.5	1.48	3.0	7.40	7.50	"	45.08	3.60	0.81	0.964	1.23
	369	275.1	1.48	3.2	7.45	7.60	"	45.85	3.84	0.88	0.962	1.14
	371	269.1	1.48	3.2	7.40	7.50	"	44.85	3.84	0.86	0.962	1.16
	372	273.0	1.48	3.2	7.40	7.50	"	45.50	3.84	0.87	0.962	1.15
	387	272.8	1.48	3.0	7.40	7.45	"	45.47	3.60	0.82	0.964	1.22
D-4	360	274.0	1.48	3.1	7.55	7.60	0.25	45.67	7.44	0.85	0.926	1.18
	368	271.3	1.48	3.3	7.60	7.65	"	45.22	7.92	0.90	0.921	1.11
	373	271.7	1.48	3.2	7.50	7.55	"	45.28	7.68	0.87	0.923	1.15
	375	273.9	1.48	2.9	7.60	7.70	"	45.65	6.96	0.79	0.930	1.27
	385	268.6	1.48	3.0	7.45	7.50	"	44.77	7.20	0.81	0.928	1.23
	386	271.7	1.49	3.1	7.65	7.80	"	45.28	7.44	0.84	0.926	1.19
D-5	370	271.6	1.47	3.2	7.35	7.40	0.125	45.27	15.36	0.87	0.846	1.15
	377	270.2	1.48	2.8	7.35	7.40	"	45.03	13.44	0.76	0.866	1.32
	379	272.0	1.48	2.9	7.35	7.40	"	45.33	13.92	0.79	0.861	1.27
	383	272.3	1.48	3.0	7.35	7.55	"	45.38	14.40	0.82	0.856	1.22
	384	273.7	1.48	2.9	7.35	7.45	"	45.53	13.92	0.79	0.861	1.27
	388	272.7	1.49	2.8	7.35	7.45	"	45.45	13.44	0.76	0.866	1.32

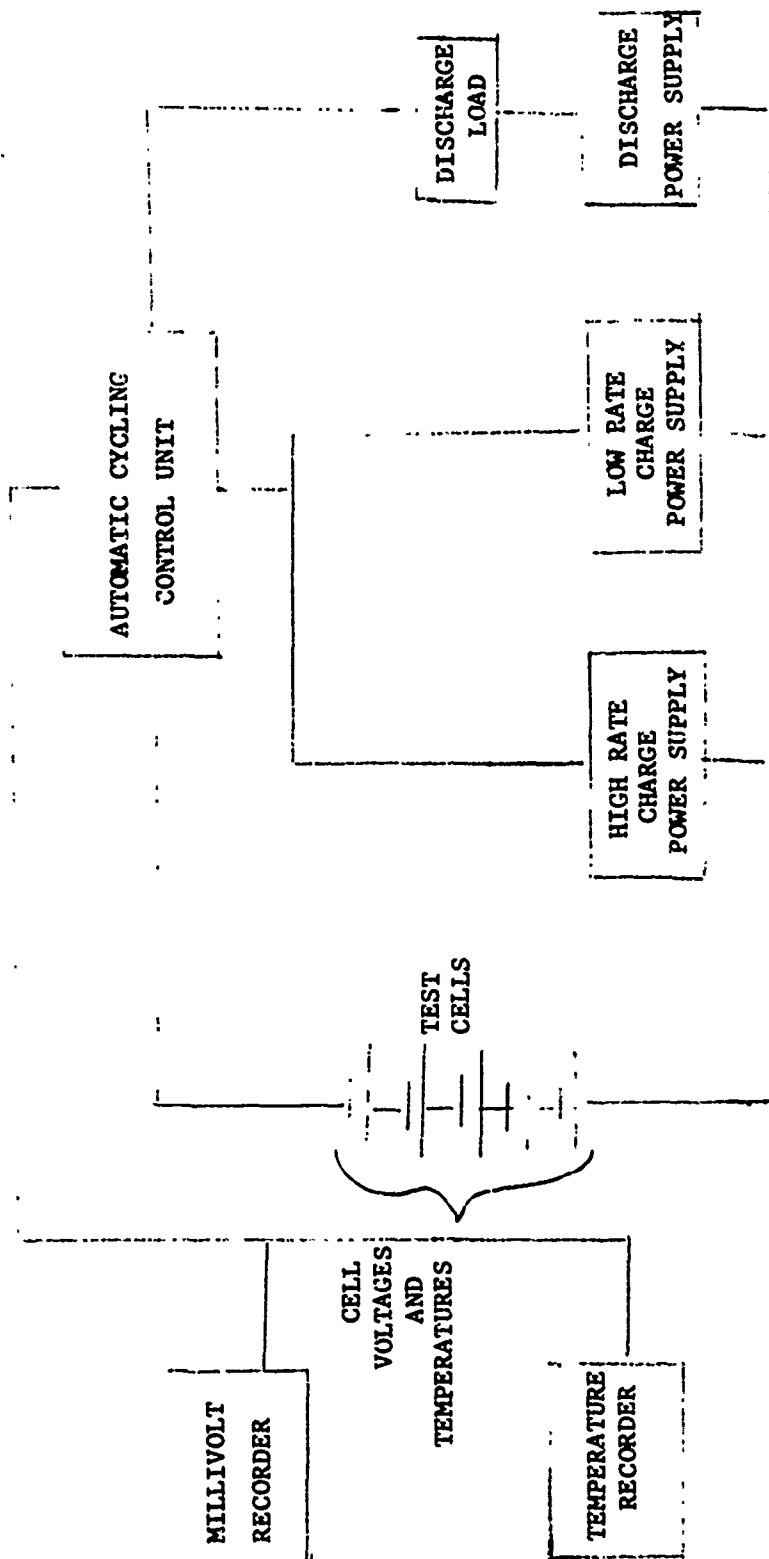


FIGURE 1. CIRCUIT DIAGRAM - TESTING APPARATUS

and charge time to the Step 1 to Step 2 switchovers, are copied onto punch card transcript forms daily. Once a week these punch card transcripts forms are transferred to the Computer Science Center at WPAFB for card punching and then computer analysis. The computer analysis consists of calculating the individual cell qualities, an average group quality, and a group charging voltage quality. The computer program then prints out the results of these calculations along with the cycle number, discharge current, and recording date for each group by ascending cycle number. Once 200 cycles of data have been accumulated for a group, average-cell-quality-values-versus-cycle, and group-charging-voltage-quality-versus-cycle plots are made.

A new definition of electrical discharge quality was developed for these tests. This new definition is:

$$Q_E = \frac{E_{eod} + IR}{ngIR} \quad (10)$$

where E_{eod} = the end-of-discharge voltage,
 I = the discharge current in amps,
 R = the initial internal resistance in ohms,
 n = the number of hours required to fully discharge the cell at Current I , and
 g = the specific capacity of the cell in grams per amp-hr.

This definition of quality has units of amps/gram. The definition was developed such that it tends to be independent of charge or discharge rate and cell size. The only experimental parameters left to assign for real quality measurements are (1) the temperature and (2) the depth of discharge. The manufacturer's rated capacity was used to determine the values of I , g , and the depth of discharge. The actual capacity could have been used since the n and I exactly compensate one another in the quality calculation. The values required for individual cell quality measurements are given in Table IV and V. The individual cell failure qualities are also calculated by Equation (10), except that 1.00 volt, compensated for IR , was used instead of the end-of-discharge voltage (E_{eod}).

Although the quality in Equation (10) is directly proportional to a corrected end-of-discharge voltage, there are several important reasons for retaining the term "quality". The first reason deals with the conceptual basis for quality and a need to measure both initial values and their rates of degradation. A history of requirement: for the development of a quality equation are presented in a special

report "Rate of Discharge for Accelerated Life Tests of Nickel-Cadmium Cells". (10)
The second reason for using quality deals with the necessity of comparing the results of one test with the results of another. The need for having to specify such things as cell sizes, charging rates, and discharging rates have been taken into account with the use of quality as defined in Equation (10).

The previously mentioned "group charging voltage quality" was calculated by:

$$Q_{cv} = \frac{\text{amps} \times \text{time}}{\text{AH}} \quad (11)$$

where amps = Step 1 constant charging current in amps,
 time = time in hours required to reach the Step 1 to Step 2
 switchover point, and
 AH = ampere-hours removed during cycling tests.

This group quality was used in order to help relate the experimental results to a theoretical framework for accelerated life tests.

Test Results

Table VI lists the status of the verification test groups as of June 7, 1972. All cell groups listed as cycling are actually on open circuit awaiting safety features to be added to the cycling apparatus. Once the safety features have been added, the cycling of these groups will be resumed.

Group C-3 failed because of mechanical problems in the cycling equipment. The discharge relay for this cycling rack stuck closed during the discharge of Cycle 244. As a result, the cells were subjected to an additional discharge of about 335 ampere-hours before the group was manually put on open circuit. All cells had burst their retaining plates and Cell 765 had ruptured. A small hole was drilled into each cell to relieve the pressure buildup. All cells are stored in plastic bags awaiting further examination.

Two cells (752 and 772) of Group C-1 also burst their retaining plates. Preliminary investigations indicated the group was subjected to the high rate (48.0 amperes) of charge for the entire 3-hour charge period. This overcharge appears to have happened during Cycles 94, 95, and 96 before the group was open circuited. There appeared to have been no other equipment malfunctions.

TABLE VI. SUMMARY OF VERIFICATION TEST GROUPS AS OF JUNE 7, 1972

Group No.	Charge Current, <u>amp</u>		Discharge Current, amp	Status, cycles
	High	Low		
<u>Charge Strain-Rate Test</u>				
C-1	48.0	2.0	7.5	Cycling (97)
C-2	24.0	2.0	7.5	To be started
C-3	12.0	2.0	7.5	Failed (244)
C-4	6.0	2.0	7.5	Cycling (791)
C-5	3.0	2.0	7.5	Cycling (1508)
<u>Discharge Strain-Rate Test</u>				
D-1	3.0	0.6	3.0	Cycling (792)
D-2	3.0	0.6	6.0	Cycling (618)
D-3	3.0	0.6	12.0	Cycling (560)
D-4	3.0	0.6	24.0	Cycling (301)
D-5	3.0	0.6	48.0	Cycling (171)

A suggested explanation is that a thermal runaway condition existed in which the temperature of the cells exceeded 70 degrees centigrade during charge, and the switchover for the Step 1 to the Step 2 rate of charge was never reached. If this explanation is correct, the failure mechanism may be different from that expected at normal charging rates, and a limit on stress levels may have been identified for the first time on this research program. If poor controls were responsible for the thermal runaway, then the test conditions were changed rather than a limiting failure mechanism. Investigation of the occurrence surrounding this problem are continuing.

The results of the verification tests to date were used for preliminary estimates of the acceleration factors for the various groups. These preliminary results are listed in Table VII. Since the degradation of cell quality does not appear to be linear, the acceleration factors listed in Table VII are expected to change with cycling. As a result, an in-depth analysis of the data was not performed for this report.

Several points concerning the data in Table VII need to be discussed as follows: (1) The data indicate that both the Charge Strain-Rate Test and Discharge Strain-Rate Test should lead to valid accelerated tests. (2) The results of Group D-3 appear inconsistent with other groups the test. An examination of the data showed experimental test problems which will need to be analyzed with regard to the data. However, a separate entry was made in Table VII which shows that Group D-3 had the same change in quality but that it occurred in only half as many cycles. If this correction is used, the overall trend becomes self-consistent. (3) The acceleration factors are based on only two points per group and therefore will require further data and physical analysis. (4) The results listed in Table VII were obtained without the data manipulations required of previous tests.^(9,10) These encouraging results imply significant improvements have been made in the operations involved in both testing and in data collection.

Failure Analysis

A failure analysis will be performed on all failed cells in order to demonstrate that the failure mechanism at a higher stress level is the same as the failure mechanism at the lower, or normal, stress level. Table VIII lists a failure analysis procedure which is recommended for use on the cells from the Charge Strain-Rate and Discharge Strain-Rate tests. This procedure should provide the data required to determine failure determinates. After the failure determinates, the failure mechanisms should be determined. The results of the failure analysis procedure should also assist in this determination of mechanisms.

TABLE VII. PRELIMINARY ESTIMATE OF ACCELERATION FACTORS FOR VERIFICATION TEST GROUPS

Group No.	Step 1 Charge, amp	Average Initial Q	Average Q at Last Printout	Cycles Between Initial and Last Printout	Change in Q Units Per Change in Cycles	Acceleration Factor
<u>Charge Strain-Rate Test (20 amp-hr Cells)</u>						
C-1	48.0	0.495	0.474	94	0.000223	13.9
C-2	24.0					
C-3	12.0	0.493	0.477	234	0.000068	4.3
C-4	6.0	0.506	0.488	780	0.000023	1.4
C-5	3.0	0.487	0.463	1,495	0.000016	1.0 ^(a)
<u>Discharge Strain-Rate Test (6 amp-hr Cells)</u>						
D-1	3.0	1.580	1.504	780	0.000098	1.0 ^(a)
D-2	6.0	1.486	1.405	598	0.000152	1.5
D-3	12.0	1.440	1.388	546	0.000095	1.0
D-4	24.0	1.431	1.285	286	0.000510	5.2
D-5	48.0	1.435	1.285	168	0.000893	9.1
D-3	12.0	1.440	1.388	277	0.000188	1.9

(a) Acceleration factor indexed at 1.0 to represent "normal" operating conditions.

TABLE VIII. FAILURE ANALYSIS PROCEDURE FOR CELLS IN VERIFICATION TESTS

1. Physical Examination

- 1.1 Remove retainer plates, weigh cell, compare with original weight
- 1.2 Check leak, use 0.25 percent phenolphthalein solution

2. Electrical Performance

- 2.1 Replace retainer plates, measure open-circuit voltage
- 2.2 Measure internal resistance
- 2.3 Discharge at C/2 rate to 1.0 volt using the manufacturer's rated capacity
- 2.4 Charge at C/10 for 24 hours with 1.50-volt limit, record time to 1.50 volts or voltage after 24 hours
- 2.5 Repeat 2.3
- 2.6 Repeat 2.4
- 2.7 Repeat 2.5
- 2.8 Check for internal shorts by:
 - (a) Discharge through 1-ohm resistor until cool
 - (b) Short terminals for 16 hours
 - (c) Charge 5.0 minutes at C/10 rate
 - (d) Read open-circuit voltage immediately and after 24-hour stand.A decay of more than 0.10 volt indicates possible short.

3. Disassembly

- 3.1 Remove cell (can avoiding damage to internal components; note any irregularities
 - 3.2 Place electrode pack in Soxhlet extractor and extract the electrolyte for 48 hours under nitrogen atmosphere. Analyze the extracted electrolyte for KOH and K_2CO_3 by titrating with standard 1.0 N acid.
 - 3.3 After removing the electrode pack from the extractor, dry the pack at 60 C for 24 hours. Weigh the dry pack.
 - 3.4 Place electrode pack between Lucite retainer plates clamped to hold the cell tightly compressed. Place pack in beaker with sufficient 30 weight percent KOH to cover electrodes and separators. Allow pack to soak for 24 hours. Charge at C/3 rate for a time equal to 1.5 times the discharge time of 2.7.
 - 3.5 Discharge at C/2 rate in flooded state. Record potentials of positives and negatives against Hg/HgO reference electrode as function of time during discharge. Continue discharge until both sets of electrodes have been fully discharged.
 - 3.6 Disassemble electrode pack and note any irregularities such as burned or discolored separator and damaged electrodes.
-

During charge or discharge of sealed cells, the major portion of gradients of pressure, voltage, temperature, or concentration tends to exist between electrodes. Therefore, it is reasoned that thicker electrodes will allow more efficient use of active material over a longer period of time because the number of gradients will be decreased and the severity of gradients will be essentially unchanged. For the same reason, the physical strains of depth of discharge, heat content, volumes of gas, and charge densities can be increased without any commensurate increase in degradation rates. The thicker substrates and moderate pore filling both have to do with mechanical stresses. It is well known, for example, that cadmium expands 230 percent in going to cadmium hydroxide. Room must be allowed for this expansion to take place. A moderate pore filling will allow a more effective use of material that is present without commensurate stress and strain on the mechanical structure of the porous electrodes. The prolonged final washing of electrodes to eliminate carbonate should also enable the thorough removal of nitrate. Preliminary tests on this program, using commercial electrodes, showed a great deal of difficulty with the "nitrate shuttle". For longer life cells, the extra precautions of removing all carbonates and nitrates cannot be over emphasized. With regard to electrodes matching on the basis of impregnation weight gains, it was reasoned that not all of the active materials impregnated into electrodes are ever available as an electrical capacity. Consequently, two electrodes which showed the same electrical capacity but differed in weight gain would have a substantial difference in pore filling or a substantial difference in some other property which limits the access to this active material. It seemed logical to expect that if cells were matched on both electrical and weight capacities, that the physical performance of electrodes in a cell would tend to be more identical and therefore a combination of electrodes would tend to be longer lived. Polypropylene separator was suggested because nylon separators have been found to oxidize particularly under over-charge conditions. Separator oxidation is the main source of carbonate pickup during use of sealed cells and polypropylene is relatively stable to oxidation. The solid-nickel components and mercury-grade potassium hydroxide are recommended because metallic and ionic impurities are to be avoided in any cells having long life.

The fabrication of these longer life cells was described in detail in the Second Annual Report.⁽¹⁸⁾ Plaques were made 0.060 inch thick with Type 287 carbonyl nickel powder. The plaques were impregnated with nickel or cadmium hydroxide using a standard vacuum impregnation technique followed by cathodic polarization. Five impregnation cycles were used for each electrode. The impregnated electrodes were formed in excess 30 weight percent KOH containing 0.1N LiOH. After the formation cycles were completed, the electrodes were washed with 40 changes of deionized water to insure complete removal of the KOH electrolyte so as to prevent any subsequent formation of K_2CO_3 . The electrodes were stacked between layers of filter paper and vacuum dried for 3 days at 60 C.

The 3.0 x 6.0 x 0.060-inch plaques had an average weight of 35.8 grams. Their average porosity was 78.0 percent with a standard deviation of 0.9 percent. The average weight gain after five impregnation cycles for the cadmium electrodes was 26.9 grams with a standard deviation of 1.1 grams. The average weight gain after five impregnation cycles for the nickel electrodes was 15.8 grams with a standard deviation of 0.9 gram. These figures correspond to a loading of 2.12 grams of $Cd(OH)_2$ per cm^3 of pore volume for the negative electrodes and 1.25 grams of $Ni(OH)_2$ per cm^3 of pore volume for the positive electrodes. These loadings are slightly higher than the loadings of 1.75 and 1.0 gram per cm^3 of pore volume used by Fleischer for the negative and positive electrodes respectively.⁽¹⁹⁾ The loadings in the present work correspond to 44.4 percent of the porous volume filled with $Cd(OH)_2$ of density 4.79 g/cm^3 and 31.8 percent filled with $Ni(OH)_2$ of density 3.94 g/cm^3 .⁽²⁰⁾ By comparison, the loadings of commercial cells calculated from tear-down analysis data⁽⁴⁾ were from 50 to 58 percent of the pore volume filled with $Cd(OH)_2$ and from 42 to 55 percent of the pore volume filled with $Ni(OH)_2$. The lighter loading of the electrodes for use in the cells designed to have increased life fulfills the third item above "moderate pore filling to lower mechanical stresses".

Cells in Hermetically Sealed Cases

A small number of cells were fabricated in hermetically sealed cases to demonstrate the capability for complete cell fabrication at the Aero Propulsion Laboratory. These cells were assembled in stainless steel cans with nickel seal covers. The cans and cover assemblies (part numbers 201A3019-22 and

152B504AD-1, respectively) were purchased from the Battery Business Section of the General Electric Company. Figure 2 shows a drawing of the cell and its assembly details.

The sintered nickel plaques used in these electrodes had dimensions of $2.5 \times 6 \times 0.060$ inches. Their average porosity was also 78 percent. The average weight gain after five impregnation cycles was 23.1 grams for the negative electrodes and 11.3 grams for the positive electrodes. These figures correspond to a loading of 2.56 grams of $\text{Cd}(\text{OH})_2$ per cm^3 of pore volume of the negative electrodes and 1.26 grams of $\text{Ni}(\text{OH})_2$ per cm^3 of pore volume of the positive electrodes. Expressed as percent of the pore volume filled, these figures correspond to 53.7 percent for the negative electrodes and 32.0 percent for the positive electrodes. Each of these impregnated master plaques was cut into three electrodes after they were formed in 30 weight percent KOH.

Electrolyte Volume in Sealed Cells. The decision of how much electrolyte to use in a sealed nickel-cadmium cell which operates in a starved electrolyte condition requires a number of considerations. If too little electrolyte is used, the cell will have a high internal resistance and a low ampere-hour capacity. If much electrolyte is used, high internal pressures may occur because the rate of oxygen recombination is decreased. Lunn and Parker⁽²¹⁾ have studied this problem of how much electrolyte to add to sealed nickel-cadmium cells. They found that the amount was critical to maintain both low internal resistance and low internal pressure during charging. The optimum amount of electrolyte in their study was equal to the volume that filled the pores of the plates plus about 25 percent of the total quantity retained by the separator after immersion in the electrolyte and draining off the surplus. Care must be taken in the use of such a rule of thumb because the state of charge was not given by Lunn and Parker. Fleischer⁽²²⁾ has stated that the rule of thumb for batteries for space applications which contain polypropylene separators is to use a weight of electrolyte equal to 17 percent of the element weight. All such rules of thumb imply that certain other parameters of cell design such as porosity, loading, and amount of separator are within certain limits for the rules to be valid.

The average total weight of the elements in the demountable improved cells (three negative electrodes, two positive electrodes, plus separator) was 175 grams. The volume of 30 percent KOH of density 1.285 g/cm^3 which correspond to various percents of the element weight are

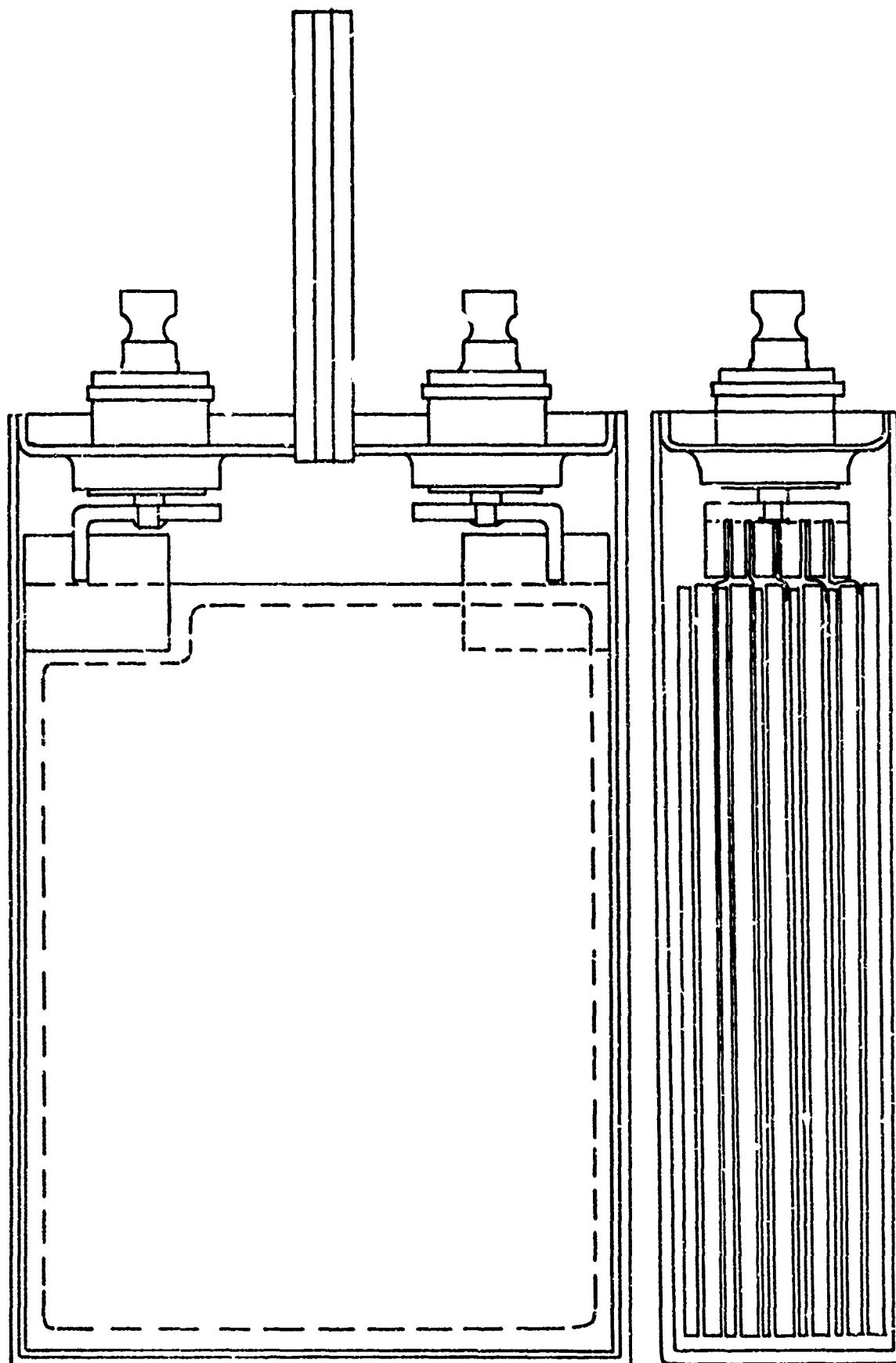


FIGURE 2. DESIGN OF HERMETICALLY SEALED NICKEL-CADMIUM CELL

Percent of Element Weight

Volume of 30% KOH, cm³

15	20.2
16	21.8
17	23.2
18	24.4
19	25.8

The demountable improved cells were filled with 20.0 cm³ of 30 weight percent KOH. According to the rule described above for calculating the quantity of electrolyte (17 percent of the element weight), this was too little electrolyte. However, in view of the fact that the electrodes in these cells were more lightly loaded with active material than most commercial cells, it was felt that slightly less electrolyte would be required.

The elements of these cells were almost dry to the touch when the cells were disassembled during subsequent failure analysis. Furthermore, as is discussed in connection with failure analysis, one cell which was inadvertently filled with about 25 cm³ of electrolyte instead of 20 cm³ had a slightly lower initial internal resistance and did not fail during its evaluation. For these reasons the hermetically sealed improved cells should be filled with 25.0 cm³ of 30 weight percent KOH. A volume of 25.0 cm³ of 30 percent KOH would constitute 18.4 percent of the element weight in the hermetically sealed improved cells.

Evaluation of Longer Life Cells

Cells in Demountable Cases

Four groups of five cells were selected and matched for evaluation. One of the groups was evaluated at each of the following temperatures: 40 C, 25 C, 10 C, and -5 C. The cycling regime for all four groups was the same. Cells were charged at the C/2 rate until the group voltage averaged 1.45 volts per cell at a temperature of 25 C. After reaching this voltage, the cells were switched to the C/10 charge rate for the remainder of a three-hour charge period. The switch-over voltage was compensated for temperatures other than 25 C using a temperature coefficient of -0.45 mV/deg C. Discharge was at the C rate for one-half hour, followed by one-half hour of open circuit stand. Thus, the total cycle time was four hours, three hours of charge, one-half hour of discharge, and one-half hour of open circuit stand. Cell failure was defined as the cell's voltage falling

below 1.1 volts, compensated for temperature and internal resistance, before the end of the specified discharge time.

Cells were removed from test at the end of discharge after they had failed. It was planned that cycling of a group of cells would be terminated when four cells had failed. However, since the cycling equipment was required for the verification tests before all four groups had failed, the evaluation of the demountable improved cells was terminated before all groups had failed. Nevertheless, it was shown that the improved cells had longer cycle lives than did cells used for the temperature experiment under the same conditions. Following is a summary of the results of the evaluation of the demountable improved cells and the temperature-experiment cells made with commercial electrodes.

<u>Operating Temp., C</u>	<u>Cycles to Failure Temp-Experiment Cells (a)</u>	<u>Cycles to Failure Improved Cells</u>
40	12	25 ^(a)
25	257	1169 ^(a)
10	163	575 ^(b)
-5	81	772 ^(b)

(a) Test completed - four failed cells.

(b) Test terminated - two failed cells.

Failure Analysis. The following abbreviated failure analysis procedure was used in the demountable improved cells which failed during evaluation.

(1) Physical Examination

1.1 Weigh cell, compare with weight obtained after assembly.

1.2 Check leak, visually, by observing any crusty deposits.

(2) Electrical Performance

- 2.1 Measure open circuit voltage.
- 2.2 Measure internal resistance.
- 2.3 Measure capacity of each set of electrodes according to the following procedure. Charge at C/2 to replace exactly the capacity removed during the last discharge on test. (Since cells were removed from test at the end of discharge cycle and the depth of discharge was 50 percent, the charge time required in this step was one hour.) Record the potentials of both electrodes with respect to the cell case as a reference electrode during charge. Discharge at C/2 rate until both electrodes are completely discharged as indicated by their potential-time curves with respect to the case reference electrode. Determine the limiting set of electrodes, their capacity, and the excess capacity of the other set.
- 2.4 Check for internal shorts by (a) short cell terminals for 16 hours, (b) charge at C/10 for 5.0 minutes, (c) read open circuit voltage immediately and after 24 hour using a meter with an impedance of at least 100,000 ohms/volt. A decay of more than 0.10 volt indicates a possible internal short.

(3) Disassembly

- 3.1 Open cell and remove cell element (electrode and separator stack). Examine for burns, broken tabs, or other signs of damage.
- 3.2 The element from the last cell which fails in each group will have its electrolyte extracted in a Soxhlet extractor and analyzed for KOH and K_2CO_3 . The weight of the dry separator after extraction will be compared with the initial separator weight.
- 3.3 The separator from cells other than the last to fail in each group will be removed from the element after Step 3.1 and washed in deionized water and dried. Its weight will be compared with its initial weight.

Due to lack of time and funds, the complete failure analysis described above was not performed on all the cells. In most cases, only the physical examina-

tion and electrical performance portions were performed. The data obtained during failure analysis are given in Tables IX, X, XI, and XII.

The data in these four Tables do not always indicate that a cell was a failure because the capacities of both electrodes are greater than the 90 amp-minutes required for discharge during cycling. However, these capacities are measured to the knees of the discharge curves of the individual electrodes and include capacity that was available for discharge at a voltage of less than 1.10 which was specified as the failure limit. For example, Cells 203, 210, and 213 in Table X all have capacities greater than 90 amp-minutes, but their capacities to a cell voltage of 1.10 were

<u>Cell</u>	<u>Capacity to 1.10 volts, amp-min</u>
203	85.5
210	88.5
213	96.0

Since the cells were required during test to provide 90 amp-min at a voltage greater than 1.10, Cells 203 and 210 had definitely failed. Cell 213 would not be considered a failure during the failure analysis procedure since it provided 96 amp-min at a voltage greater than 1.10 volts. However, the cell could possibly have recovered during the time after it was removed from cycling so that it met the requirements during failure analysis even though it did not meet them during cycling.

During discharge, the potentials of both electrodes in each cell decreased with respect to the stainless steel case used as a reference electrode. The decreases of electrode potential from the start of discharge until the cell voltage reached 1.10 were

<u>Cell</u>	<u>Decrease in Electrode Potential</u>	
	<u>Negative, volts</u>	<u>Positive, volts</u>
203	0.08	0.24
210	0.05	0.24
213	0.05	0.24

TABLE IX. FAILURE ANALYSIS DATA FOR DEMOUNTABLE IMPROVED CELLS
EVALUATED AT 40 C

Cell	202	205	208	221	224
Cycles to Failure	7	8	25	7	NF
Weight Change, g	+0.4	0.0	-0.2	0.0	-2.4
Open Circuit Voltage	1.17	1.21	1.22	1.10	1.18
Internal Resistance, milliohms					
Before Cycling	8.8	6.5	7.7	4.8	5.1
After Cycling	21.3	16.1	16.8	10.9	5.0
Positive Capacity, amp-min	68.3	87.0	114.0	108.0	80.3
Negative Capacity, amp-min	208.5	243.8	303.0	81.0	606.8
Voltage Loss During Internal Shorts Test	0.62	0.18	0.17	0.85	0.14
Electrolyte Analysis					
KOH, g			8.60		
K ₂ CO ₃ , g			0.80		

TABLE X. FAILURE ANALYSIS DATA FROM DEMOUNTABLE IMPROVED CELLS
EVALUATED AT 25 C

Cell	201	216	203	210	213
Cycles to Failure	317	317	1,169	1,169	1,169
Weight Change, g	-0.2	-0.6	-0.7	-0.6	-0.5
Open Circuit Voltage	1.26	1.24	1.25	1.28	1.27
Internal Resistance, milliohms					
Before Cycling	7.8	9.2	8.7	11.3	9.7
After Cycling	46.1	156.0	17.6	10.2	11.1
Positive Capacity, amp-min	90.0	137.0	159.0	141.0	164.3
Negative Capacity, amp-min	210.0	69.0	288.8	347.3	422.3
Voltage Loss During Internal Shorts Test	--	0.52	0.21	0.16	0.07

TABLE XI. FAILURE ANALYSIS DATA FOR DEMOUNTABLE IMPROVED CELLS
EVALUATED AT 10 C

Cell	206	214	2J4	212	218
Cycles to Failure	236	236	575 (NF)	575 (NF)	575 (NF)
Weight Change, g	-0.3	-0.2	-0.5	0.0	-0.8
Open Circuit Voltage	1.23	1.26	1.23	1.23	1.22
Internal Resistance, milliohms					
Before Cycling	5.1	7.1	4.4	8.7	7.3
After Cycling	9.1	8.7	3.1	6.5	7.9
Positive Capacity, amp-min	87.0	163.5	94.5	106.5	106.5
Negative Capacity, amp-min	315.8	385.5	274.5	307.5	420.0
Voltage Loss During Internal Shorts Test	0.77	0.36	0.08	0.64	0.35
Electrolyte Analysis					
KOH, g		8.24			
K ₂ CO ₃ , g		1.11			

TABLE XII. FAILURE ANALYSIS DATA FOR DEMOUNTABLE IMPROVED CELLS
EVALUATED AT -5 C

Cell	207	215	211	217	213
Cycles to Failure	341	361	772 (NF)	772 (NF)	772 (NF)
Weight Change, g	+0.2	+0.1	-0.5	0.0	-0.8
Open Circuit Voltage	1.24	1.24	1.26	1.26	1.26
Internal Resistance, milliohms					
Before Cycling	4.5	7.9	6.6	3.3	4.1
After Cycling	5.6	7.2	4.5	2.7	2.2
Positive Capacity, amp-min	170.3	162.0	177.0	159.0	192.0
Negative Capacity, amp-min	356.3	336.0	381.0	304.5	550.5
Voltage Loss During Internal Shorts Test	0.31	0.83	0.13	0.91	0.06
Electrolyte Analysis					
KOH, g		7.77			12.11
K ₂ CO ₃ , g		1.76			1.04

These data lead to the conclusion that the failure determinant for these three cells was loss of potential at the positive electrode. The electrodes still had sufficient capacity as shown in Table X, but it was available only at a potential below that required by the cycling conditions. Similar behavior was observed in other cells used in the evaluation of demountable improved cells.

The electrolyte analyses show a slight increase in K_2CO_3 concentration over the electrolyte that was used to fill the cells. The K_2CO_3 concentrations in the electrolytes extracted from the cells after evaluation are in the range of 40 to 90 g/l whereas the electrolyte with which the cells were filled had a K_2CO_3 concentration of 9.5 g/l. The increase in carbonate evidently came from carbonate formed in the electrodes during prior operations even though precautions were taken to minimize carbonate formation.

The analysis of Cell 219 evaluated at $-5^\circ C$ showed that it was filled with more than 20 cm^3 of electrolyte. Its internal resistance was the second lowest prior to cycling and the lowest after cycling. Also it had not yet failed when its evaluation was terminated. These facts suggest that the electrolyte volume used in the demountable improved cells was somewhat less than optimum.

Conclusions and Recommendations

The performance of the improved demountable cells was shown to be superior to that of the cells used in the earlier Electrical Stress-Rate of Strain and temperature experiments. This improvement in performance is thought to be the result of at least 3 improvements: (1) polypropylene separators, (2) techniques to minimize chemical impurities, and (3) thicker electrodes in the cells.

The same improvements were incorporated into the hermetically sealed cells assembled at APL. Thus they are expected to have cycle lives similar to the demountable cells when operated under the same conditions. Based solely on the problem encountered during assembly, two changes are recommended in the design of the hermetically sealed cells. (1) The width of the nickel combs as shown in Figure 2 should be increased from one-half inch to approximately 0.65 inch to make it stronger and less subject to deformation during assembly of the electrode tabs into the slots in the comb. (2) The height of the tabs on the outermost electrodes should be increased sufficiently so that the tabs of these electrodes can fit well into the slots in the combs. This means that the tabs for the outermost electrodes must be higher than the tabs on the inner

electrodes before assembly so that after assembly the bottoms of all electrodes will be properly aligned. Detailed measurements and drawings will be required in order to determine the correct height of tab for each electrode.

Evaluations. The performance of the hermetically sealed improved cells will need to be evaluated and compared with the performance of commercial 6 ampere-hour cells by APL personnel or as part of a separate effort. The charge-discharge regime planned for the evaluation is a typical near earth orbital profile. The test temperature is to be 20 C. The total time per orbit for this regime is 110 minutes of which 35 minutes is discharge and 75 minutes is charge. A 50 percent depth of discharge is desired. Thus, the discharge rate must be $6/7$ C in order to discharge 50 percent of the cell capacity in 35 minutes. Charging is to be done at a constant current $C/2$ rate to a voltage limit selected on the first cycle followed by a trickle charge at a $C/10$ for the remainder of the 75 minute charge time. The voltage limit selected on the first charging cycle will be that group voltage obtained after exactly 1 hour of charging at a $C/2$ rate.

TASK III. SUPPORTING STUDIES

Any research program which seeks to develop accelerated life tests for objects as complex as sealed spacecraft batteries will require a great deal more than a few simple experiments to establish valid tests. A theoretical basis is necessary to gain acceptance of results by electrochemists and by other physicists and physical chemists. A large amount of reliable data will be desired. Ancillary knowledge such as thermophysical properties and statistical methods must be considered and taken in account. A cognizance of relevant published literature is more or less assumed to be a part of a research program. Therefore, this section of the Final Report is to summarize some of the activities and accomplishments from studies to support the main efforts described as Tasks I and II of this program.

Task III (a). Facility Maintenance

The maintenance program developed for the Battery Section of the Aero Propulsion Laboratory at WPAFB has been described previously.⁽²³⁾ The purposes of the program were to have each piece of equipment in a state of readiness to perform its intended functions with a minimum amount of preuse conditioning; to reduce the number of equipment failures; and to provide for speedy repair when failures did occur.

A program was developed which consisted of the following four inter-related parts: (1) record of service--this consisted of a card-file system with an entry for each piece of equipment. This system provided a means of reviewing the history of a piece of equipment for regular and emergency services and for deciding to continue to repair or to replace the item; (2) schedule of repetitive services--a schedule was developed which provided the periodic maintenance and service required by the various pieces of equipment in the system; (3) service procedures--written service procedures were provided for each group of equipments. These procedures included a list of steps for the servicing routine and emphasized any feature that required special attention; and (4) inventory of spare parts--an inventory of spare parts was maintained to provide a list of components available and as an indicator of when to purchase additional parts.

The system was later expanded to include a schedule and record of the calibration service performed on equipment in the Battery Section by another group at APL. This additional section of the maintenance program included a listing of all items which required calibration, a schedule of calibration, and a record of any service or calibration performed.

Task III (b). Data Analysis

This data analysis section deals with data collected from simulated orbital life tests started under Contract AF 33(615)-3701 and continued under this contract. Two groups of cells (each consisting of 10 sealed nickel-cadmium cells) were evaluated in each of the simulated synchronous (24 hours) and polar (5.31 hours) orbital routines. Some of the synchronous orbit cells successfully completed 1471 days or orbits about the earth with 414 charge-discharge cycles during nine eclipse seasons. These cells were tested at a maximum 80 percent depth of discharge. Some of the polar orbit cells completed 929 calendar days of operation representing 4180 orbits about the earth with 1152 charge-discharge cycles during six eclipse seasons. The polar orbit cells were discharged at a maximum 40 percent depth of discharge. Two special reports^(24,25) have been published which contain all the information obtained from these orbital tests.

The special report entitled "Simulated Orbital Life Tests for Spacecraft Cells, Part I. Procedures and Manually Acquired Data"⁽²⁴⁾ contains information regarding the preparation and matching of cells for life tests and the subsequent life-testing routines for the sealed nickel-cadmium cells in simulated synchronous and polar orbital applications. In essence, this Part I report contains all the manually acquired data such as capacity determinations, internal resistance measurements, and failure analysis data. This report also describes problems associated with testing, their possible effects on the cells, and what corrective actions were taken. The failure analysis studies showed an increase in carbonate level over uncycled cells and even over cells which had been cycled but had not failed. It is believed that the increased carbonate levels were a result of oxidation of the separators by the charged positive electrodes.

The second special report entitled "Simulated Orbital Life Tests for Spacecraft Cells, Part II. Automatically Acquired Data, Review and Recommendations"⁽²⁵⁾

describes the content, availability, and recommended procedure for analysis of the data automatically acquired during 4-1/2 years of simulated orbital life testing. Analysis of the data by the empirical, statistical, and physical methods is recommended. The approach each of these methods would use is described.⁽²⁵⁾

Task III (c). Stress-Strain Models

Some of the important starting aspects of this subtask were summarized under Task I and "A Physical Basis for Accelerated Life Tests". The concluding situation is summarized in Table XIII. This supporting effort on modeling continued piecemeal through the entire program because the ideas of stress and strain are seldom generalized for use by electrochemists or in other nonmechanical subjects. Even so, important progress appears to be in the making in the sense that the third version of generalized stresses and strains in Table XIII appears to be more generally applicable than is the starting generalities in Table I. Onsager and Tribus relations appear to have all the necessary and sufficient conditions for understanding and designing suitable accelerated life tests. If something happens to batteries that cannot be handled with those fundamental relations, it appears that catastrophic events must be turned to for explaining failures. By "catastrophic event" it is meant an accidental impact or similar unpredictable event. Conversely, the Onsager and Tribus relations appear sufficient to explain any foreseeable aging processes. Even so, a large amount of additional work appears to be needed and justified. Some suggestions for further work are as follows:

- Quantitative numbers for the Onsager and Tribus coefficients need to be experimentally determined. Special and careful experimentation will be required.
- The use of three-dimensional stress, strain, strain-rate, and inertial mass concepts for surface tension and other surface phenomena need to be explored.
- A correction for gaseous viscosities needs to be studied further as a more correct explanation for deviations from the ideal gas law than is the present use of "Van der Waal forces". The fact that gas-viscosities do not approach zero values at zero pressure needs to be explained.
- Appropriate amount factors and intensity factors for thermal energy need to be established. The concepts of temperature

TABLE XIII. THIRD VERSION OF GENERALIZED STRESS-STRAIN AND STRESS-STRAIN RATE RELATIONSHIP

	(1) Energy Form(a)	(2) Amount Factor(h)	(3) Intensity Factor(c)	(4) Spring Analog of Strain(d)	(5) Spring Analog of Stress(d)	(6) Dashpot Analog of Strain Rate(e)	(7) Dashpot Analog of Stress(e)	(8) Inertial Mass Analog(f)
Row 1	Mechanical	Volume, V	Pressure, P	$\frac{dV}{V}$	dP	$\frac{dV}{a \cdot dt}$	$\frac{dP}{dx}$	$\Delta P = k_1 \cdot \frac{d^2V}{dt^2}$
Row 2	Electrical	Charge, Q	Voltage, E	$\frac{dQ}{V}$	dE	$\frac{dQ}{a \cdot dt}$	$\frac{dE}{dx}$	$\Delta E = k_2 \cdot \frac{d^2Q}{dt^2}$
Row 3	Thermal	Heat, q	Temperature, T	$\frac{dq}{v}$	dT	$\frac{dq}{a \cdot dt}$	$\frac{dT}{dx}$	$\Delta T = k_3 \cdot \frac{d^2q}{dt^2}$
		(Momentum, mv?)	(Velocity, v?)	$\frac{dmv}{v?}$		$\frac{dmv}{a \cdot dt?}$	$\frac{dv}{dx?}$	$(\Delta v = \frac{kd^2(mv)}{dt^2?})$
Row 4	Chemical	Moles, M	Concentration, [C]	$\frac{dm}{V}$	d[c]	$\frac{dm}{a \cdot dt}$	$\frac{d[c]}{dx}$	$\Delta[c] = k \cdot \frac{d^2M}{dt^2}$

(a) Energy forms associated with performance and aging of batteries.

(b) Generalized displacements.

(c) Generalized forces.

(d) Tribus Relations: $Strain_i = \sum_{n=Row 1}^{n=Row 4} k_n(stress)_n$.(e) Onsager Relations: $(Strain Rate)_i = \sum_{n=Row 1}^{n=Row 4} k_n(stress)_n$.

(f) Generalized Inertial Forces = Generalized Accelerations.

and entropy are well established, but early controversies have never been settled. The use of "momentum" and "velocity" as proper amount and intensity factors, respectively, has been suggested.⁽⁷⁾ A concerted effort by several persons appears to be desirable for making progress in a technical field of such magnitude as thermal energy.

- Versions of stress-strain relationships should be sought that have more universal applicability than those in Table XIII.

In the mean time the various terms in Row 1 of Table XIII are related to pressure and volume relationships for gases or to pressure-volume relationships for osmotic affects through separators or through pressure-volume relationships during the expansion and contraction of active materials. In Row 2, the spring analog is related with depth of discharge whereas the dashpot analog is related to rates of discharge as measured in current densities. In Row 3, the spring analog refers to heat-capacity relationships where as the dashpot analog is related to heat-conduction phenomena. In Row 4, the chemical analogs have to do with Fick's diffusion laws. The ratio of spring and dashpot constants leads to so called time constants which characterize the rate at which steady-state conditions tend to be reached.

Task III (d). Thermophysical Properties

During this contractual period three special reports and two journal publications have described work done pertaining to temperature effects in nickel-cadmium batteries.^(9,13,14,15,16)

"An Annotated Bibliography of the Thermal Properties of Primary and Secondary Cells"⁽¹³⁾ gives complete details and condensed tabulations of published knowledge in six sections:

- Section 1. Thermal conductivity, resistance data, and resistance-capacitance networks
- Section 2. Specific heat and heat capacity data
- Section 3. Enthalpy, entropy, and temperature coefficient of EMF data
- Section 4. Heat-generation prediction and measurement
- Section 5. Thermal design of cells and batteries
- Section 6. Environmental temperature effects on cell or battery operation and life

All the information is indexed by Subject, Author, and Facility. The report, therefore, is a good resource for both designers and users of batteries.

Another special report on "The Thermal Conductivity of Sealed Nickel-Cadmium Cells" gives practical information for calculating thermal properties of cells and batteries.⁽¹⁴⁾ Conclusions of that work are summarized next, where "Types I, II, III, or IV" refer to commercial 20-ampere-hour cells from four different manufacturers.

In the x-direction (perpendicular to the plane of the electrodes) the measured conductivities of cell Types I, II, and III are in the range 0.0026 through 0.0038 cgs unit, and average 0.0030 cgs unit. The measured k_x value for cell Type IV in comparison is 0.0086 cgs unit. The predicted (calculated) average conductivity for all four types of cell is 0.0025 ± 0.0004 cgs unit. The high k_x value cell Type IV remains unexplained.

In the y-direction (parallel with the plane of the electrodes) the cell conductivities are quite dependent on the presence of gas gaps and the amount of wetted separator extending beyond the edges of the electrodes. Even so, the calculated k_y values for the Type I, II, and III cells agreed with measured values to within ± 8 percent. Values measured are in the range 0.0056 through 0.0071 cgs unit, while predicted values are in the range 0.0047 through 0.0067 cgs unit. In calculating and predicting cell thermal conductivities, the networks given in previous reports were combined with the conductivity data for individual constructional materials and with the conductivity for the "active" materials.

The thermal anisotropy of the cells, as given by the ratio k_y/k_x , varies according to cell type, and values in the range 1.76 through 2.63 are obtained. Values in the range 2.34 through 20 have been reported in the literature. It is postulated that the anisotropy of the cells is largely dependent on the presence of gas gaps at the cell edges and bottom. If large gaps exist, a low conductivity value is expected, and vice versa. Thermal-conductivity measurements can therefore identify the presence of gaps, which otherwise is difficult. Neutron radiography might be used to identify gaps, but such an application has not been found in the literature.

The conductivity of a nickel-cadmium cell appears to increase with increasing state of charge, up to full charge, in approximately a linear manner. The measured differences between discharged and 105 percent recharged cells are about 12-14 percent, and the experimental error is estimated to be about ± 5 percent. Originally it was hypothesized that the increase in conductivity of charged cells might be due to the higher proportion of metallic

cadmium (of high relative conductivity) in the charged negative electrodes. However, measurements on individual charged and discharged electrodes do not substantiate this hypothesis. Instead, the changes in conductivity of the individual electrodes are attributed to a redistribution of electrolyte.

Because most heat is usually generated during discharge, and because it is easier to measure discharged cell conductivities, the conductivity values given for discharged cells or electrodes are recommended for thermal analyses.

The thermal resistance of the heat-transfer path in the x-direction was calculated to be the lowest of any of the paths considered. A low value for R_x ensures that most of the heat generated can be dissipated by heat sinks on the yz faces (i.e., on the sides parallel with the electrodes). Therefore, these yz faces should be relatively large compared with the xz faces (cell edges). However, the present research program has shown that the measured conductivity in the y-direction is greater than in the x-direction for the cells studied. Therefore, heat extraction in the y-direction, through the xz faces, could be more efficient than in the x-direction, through the yz faces, depending upon the relative magnitudes of the xz and yz face areas, and the measured k_x and k_y conductivity values.

Experiments with six-cell battery modules show that the packing arrangement of the cells in the modules has a noticeable effect on the temperature distribution throughout the modules during cycling because of the thermal anisotropy of the cells. Thermal-resistance networks set up for the battery modules, which include the battery hardware, enable the temperature distributions throughout the modules to be estimated and the approximate overall module temperature changes to be calculated. The most efficient stacking arrangement is found to be primarily a function of the thermal anisotropy of the individual cells. However, the type of external battery or cell surfaces available for heat extraction is another important factor to be considered.

In constructing batteries, the individual cells should be thermally matched as well as electrically matched. The two thermophysical parameters which should be matched are the overall thermal resistance, R_T , and capacitance, C_T . If, in a battery, these are matched as closely as possible, then the thermal time constant for each cell (the product of R_T and C_T) will be similar also. Simple experimental procedures for determining R_T and C_T have been outlined in the special report. However, if it is not practical to perform these tests, the cells could be matched by measuring the temperature rise on discharge under some arbitrarily chosen conditions and cells showing similar temperature changes should be used in the battery if also electrically

matched. The result of thermally matching cells will be a more-balanced battery operation. All cells should be subjected to similar temperature excursions so that all cells in a battery will have a better chance of coming to a state of full charge or discharge at the same time, thus avoiding the development of electrical mismatch.

A third special report relating to thermophysical properties was the earlier mentioned report on "Temperature and Temperature Gradients for Accelerated Life Tests of Nickel-Cadmium Cells".⁽⁹⁾ Similar use of temperature information was made in the special report "Rate of Discharge for Accelerated Life Tests of Nickel-Cadmium Cells".⁽¹⁰⁾ These reports are mentioned here because the experiments described therein depended greatly on these supporting studies on thermophysical properties. Thus, the experimental cells in unmountable cases all had specially made heaters in them. Half of the cells had the heaters off and half had the heaters on, at preselected settings so that their internal temperatures were at a constant + 40 C regardless of environmental temperatures from + 40 to -20 C. The successful execution of these plans and the observed agreement between actual and predicted temperature gradients gave evidence and confidence to the "RC-Network" approach to thermal analysis for sealed cells which has been developed in this Subtask III (d).

Task III (e). Literature Review

Published information relating to nickel-cadmium and other aspects of battery technology was collected, organized, and indexed through the Battery Information Index (BII). This information effort was originally initiated under Contract AF 33 (615)-3701 and continued under the present Contract F33615-69-C-1537. Information activities during the present program resulted in the reduction of practice of those recommendations suggested in the earlier research contract.⁽²⁶⁾

Development of the BII is summarized in the following sections:

- (1) Growth and Status, (2) Subject Indexing and Purging Procedures, and
- (3) Retrieval Techniques.

Growth and Status

The Battery Information Index contains approximately 2200 documents relating to aerospace battery technology. Input is restricted to professionally selected documents containing technical information deemed useful or relevant to

TABLE XIV . SOURCE CLASSIFICATION OF BATTERY
INFORMATION INDEX (INCLUDES
BATTERY DOCUMENTS B-1 THROUGH
B-2189

U.S. Journal Articles	248
Foreign Journal Articles	140
U.S. Patents	280
Foreign Patents	84
Books	29
Government Reports	1,051
Industrial Literature	15
Symposium Papers	338
Bibliographies	4
Total	2,189

the contractual work topics. Table XIV shows a breakdown of source classifications that have yielded useful input for the BII. Approximately half of the documents in the system are government reports. Journal articles, bibliographies, symposium papers, and books of the type expected in libraries contribute an additional 35 percent. The other holdings are industrial literature and patents.

Growth of the BII is shown from statistics on index pagination as presented in Table XV. These figures refer to a hard copy version of all indexes containing approximately 50 single-spaced lines per page. The subject, author, facility, and contract numbers indexes are all given in a single-column format. The June, 1972, statistics indicate these four indexes required 163 pages and contained approximately 8,500 index entries. In addition, patent numbers are presented in a double-column format. Five pages with 2 columns per page and 50 lines per page gives about 500 index entries. Both AD- and N-Numbers are presented in a three-column format. Ten pages of 150 items per page gives 1500 index entries. The approximate total of individual entries in the June, 1972, index is $8150 + 500 + 1500$ or 10,150 index entries. The June, 1972, index provided coverage for 2189 documents. Therefore, the number of indexing terms per document averages about 4.6. Table XVI shows a comparison of average numbers of terms per document in earlier indexes. The amount of indexing has not changed significantly.

Subject Indexing and Purging Procedures

All of the subject entries presently in the index have been technically approved by professional members actively working on Air Force battery projects. The subject indexing policy adopted for the BII is: (1) Any technical member of the project may enter any or all terms he considers to be useful retrieval tools, (2) Those terms, in essence, belong to him (for as long as he is associated with the project), (3) Subject entries may not be deleted or modified without the approval of the engineer who originally entered them into the system, and (4) The resulting subject index is a list of technically approved terms that tend to be "standardized" by engineer usage rather than by a formal thesaurus.

During 1971, a monitoring procedure was initiated to provide a continuous quality control for terms listed in the subject index. In an effort to retain consistency of term format; informal memoranda were sent to project

TABLE XV . GROWTH OF BII INDEXES

Index Type	Number of Pages For Complete Index			
	July, 1970, B-1 Through B-1580	March, 1971, B-1 Through B-1814	June, 1971, B-1 Through B-1925	September, 1971, B-1 Through B-1993
Subjects	85	105	106	103
Authors	15	29(a)	29	31
Facilities	9	10	10	11
Contract numbers	5	8(a)	8	8
Patent numbers	3	3	4	4
AD-numbers	4	5	5	5
N-numbers	4	5	5	5
Totals	125	165	167	167
				178

(a) Format change - from double column to single column per page.

TABLE XVI. AVERAGE NUMBER OF INDEXING TERMS PER DOCUMENT
IN BII SYSTEM

Index Updates	Number of Pages	Number of Index Entries	Average Number of Terms/Document
July, 1970 (B-1 through B-1580)	125	7,450	4.7
March, 1971 (B-1 through B-1814)	165	9,400	5.1
June, 1971 (B-1 through B-1925)	167	9,550	4.9
September, 1971 (B-1 through B-1993)	167	9,550	4.7
June, 1972 (B-1 through B-2189)	178	10,150	4.6

members from the information specialist to seek approvals for deletion or for modifications of terms which were originally entered into the subject index. The distribution of approximately 175 memoranda resulted in over 140 approvals for term revisions and only 6 disapprovals. This method of initiating and approving indexes appears to be a practical solution to information obsolescence and redundancy. The effectiveness of this procedure is reflected in the September, 1971, index update (Table XV). Notice that the subject index contained three pages (approximately 150 terms) less than the previous revision even though index coverage was provided for an additional 179 battery documents. The reduction of index pages was accomplished by the deletion of approximately 200 terms (feedback from informal memoranda) and the addition of approximately 200 new index terms from recent inputs. Table XVII shows changes in numbers of index entries resulting from usage of purging procedures.

Consideration was given to future subject indexing procedures that would ensure high quality retrieval from larger reservoirs of information containing numerous technical areas of battery technology. The following procedures were discussed and demonstrated to technical members on the project: (1) categorical indexing, (2) permuted indexing, and (3) reduced permutation indexing. It was concluded that technical persons consider some of these procedures to be outside their area of interest. Technical persons prefer to have their own indexing formats with guidance and help from an information specialist.

Retrieval Techniques

Retrieval of information from the BII is accomplished in the following manner:

- Step 1. Identification of battery document by number from one of seven indexes provided on microfiche. The seven separate indexes include: (a) Subjects, (b) Authors, (c) Facilities, (d) Government Contract Numbers, (e) Patent Numbers (both United States and foreign), (f) AD-Numbers to Government reports, and (g) N-Numbers to Government reports. All indexes are updated quarterly.

TABLE XVII. INITIAL RESULTS OF INDEX PURGING PROCEDURES

Index Type	June, 1971, Complete Index		September, 1971, Complete Index		June, 1972, Complete Index	
	New Entries ^(a)	Deletions	New Entries ^(a)	Deletions	New Entries ^(a)	Deletions
Authors	100	0	5	0	123	0
Facilities	19	0	5	0	25	0
Subjects	257	32	200	188	284	142
N-numbers	19	0	16	0	16	0
AD-numbers	10	0	13	0	12	0
Patent numbers	33	0	36	0	33	0
Contract numbers	10	0	4	0	13	0

(a) New entries are completely new indexing terms and are not to be considered as additional B-numbers added to previously existing terms.

Step 2. Verification of selected battery document from total Accessions List on microfiche or from abstract card files.

Step 3. Retrieval of document by B-Number from microfiche report file or from hard-copy document file.

Users develop a skill in retrieving information from the BII as they gain familiarity and experience with the system. A given battery document may be retrieved through any of the above seven indexes depending upon the starting information. While it is true that any of several indexes will deliver the needed B-Number, it is also true that usage of combined indexes will provide B-Numbers faster depending upon the amount of available starting information. Retrieval of battery information by usage of combined indexes is described in detail on pages 73-76 of Technical Report AFAPL-TR-70-44 Part II. (18)

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APPENDIX A

RECOMMENDED CELL DESIGN FOR MAXIMUM PERFORMANCE AND LIFE RECOMMENDED ACCELERATED TEST PROCEDURE

This appendix is written in fulfillment of that part of paragraph 2.6 of the statement of work which states "submit as appendixes to the Final Report, a 'Cell Design for Maximum Performance and Life' and an 'Accelerated Test Procedure'". Even though the experimental verification tests have not been completed, the recommended cell design and test procedures are based on information received to date from this program.

The recommended design of cell's is described in this report under the section entitled "Task II. Increased Battery Life". As explained in that Task II section, the fabrication of the cells is described in detail in the Second Annual Report⁽¹⁸⁾ pages 32 through 35. Although the specifications given are for 6-ampere-hour hermetically sealed cells, the actual dimensions will depend upon the size of cell required to fulfill the power requirements given for the typical near-earth orbital profile previously described under Evaluations in Task II.

Two changes are recommended in the previously mentioned design of hermetically sealed cells. (1) The width of the nickel combs shown in Figure 2 of this report should be increased from 1/2 inch to approximately 0.65 inch to make them stronger and less subject to deformation during assembly of the electrode tabs into the slots of the comb. (2) The height of the tabs on the outermost electrodes should be increased sufficiently so that the tabs of these electrodes can fit well into the slots in the combs. This height adjustment means that the tabs for the outermost electrodes must be longer than the tabs on the inner electrodes before assembly so that after assembly the bottoms of all electrodes will be properly aligned.

After the cells are assembled, they should be filled with a volume of 30 percent KOH (density of 1.285 g/cm^3) equivalent to 18.5 percent of their element weight. The element weight is the total dry weight of the separator and the positive and negative electrodes. The cells should stand for at least 24 hours after adding the electrolyte before proceeding with the electrochemical conditioning.

After the 24-hour stand, the cells should be subjected to the following steps to condition and set the state of charge of the cells:

- Step 1. Charge for 6 hours at C/3 rate or until a voltage limit of 1.5 is reached.
- Step 2. Discharge at C/3 rate to zero volts.
- Step 3. Charge at C/3 rate for exactly 5.0 hours and seal. Measure cell voltage within 2 minutes of end-of-charge.
- Step 4. Determine capacity by the discharge time to 1.0 volt at the C/3 rate.
- Step 5. Charge at C/3 rate for 3 hours and measure internal resistance.

The cells should then be matched into groups primarily according to the capacity determined in Step 4 above. Secondary consideration should be given to internal resistance (Step 5) and the end-of-charge voltage (Step 3).

ACCELERATED TEST PROCEDURE

The normal stress level or conditions for an accelerated life test are represented by Group 1 in Table XVIII. The remaining groups in Table XVIII represent the recommended accelerated test for a typical near-earth orbital profile.

Each group should consist of eight cells, three of which should be removed during the course of the tests. One of the three cells should be removed after its quality had degraded by one-fourth of its original-minus failure-quality. A second cell should be removed after its quality degraded by one-half and the third cell removed after its quality had degraded by three-fourths. The cells to be removed from each group should be selected randomly prior to starting the tests.

Each group should be tested in a 110-minute orbit consisting of 75 minutes of charge and 35 minutes allotted for discharge. Those groups not requiring 35 minutes of discharge should be placed on open circuit to complete the allotted 35 minutes of discharge time. All groups should be tested at a 48.7 percent depth of discharge. The charge should consist of a C/2 charge

TABLE XVIII. RECOMMENDED ACCELERATED TEST PROCEDURE
BASED ON 6-AMPERE-HOUR SEALED NICKEL-
CADMIUM CELLS

Group Number	Chamber Temperature, C	Induced Temperature Gradient, C	Charge Rate		Discharge Current, ^(a) amps	Discharge Time, min
			Step 1	Step 2		
1	20	none	C/2	C/10	5	35.0
2	20	Ditto	Ditto	Ditto	10	17.5
3	20	"	"	"	20	8.8
4	20	"	"	"	40	4.4
5	20	"	"	"	80	2.2
6	20	40	C/2	C/10	5	35.0
7	20	40	Ditto	Ditto	10	17.5
8	20	40	"	"	20	8.8
9	20	40	"	"	40	4.4
10	20	40	"	"	80	2.2

(a) Depth of discharge should be 48.7 percent for all groups.

rate to a selected group voltage limit and then a C/10 charge rate for the remainder of the 75 minute charge period. The group voltage limit should be selected on the first cycle by charging the cells at the C/2 rate for 1 hour. The group voltage after this 1-hour charge should then be used during subsequent cycles as the switchover point from the C/2 to the C/10 rate of charge.

All groups should be tested in an environmental chamber with its internal temperature set at 20 degrees centigrade. Each cell in Groups 6 through 10 should then have an induced temperature gradient supplied by an external heater. This heater should be set to provide a temperature of 40 degrees centigrade on one of the cell case slides parallel to the face of the cell's electrode pack. A heater of the type previously described⁽²³⁾ would seem to be suitable for this application.

To provide data required for analysis of this experiment, the current, group voltage, individual cell temperatures, and individual cell voltages should be recorded. Also, the charge time during C/2 rate should be measured and recorded. The cell temperatures should be measured by a thermocouple placed on the cell case side opposite the external heater. The cell voltages should be recorded within the last 20 seconds of the end of discharge. In fact, this time should be as close to the end of discharge as possible.

The C/2 charge time should be used to calculate a "group charging voltage quality" by the equation:

$$Q_{cv} = \frac{\text{amps} \times \text{time}}{\text{AH}}, \quad (\text{A-1})$$

where

amps = C/2 constant charging current in amps,

time = time in hours required to reach the C/2 to C/10
switchover point, and

AH = ampere-hours removed during cycling tests.

This calculation can be used as an indication of changes in the charging quality of the group of cells and of charging efficiencies.

Primary life predictions from the tests should be based on the "electrical discharge quality" of the cells. This "quality" should be calculated from the equation:

$$Q_E = \frac{E_{eod} + IR}{ngIR}, \quad (\text{A-2})$$

where

E_{eod} = the end-of-discharge voltage,

I = the discharge current in amps,

R = the initial internal resistance in ohms,

n = the number of hours required to fully discharge
the cell at current I , and

g = the specific capacity of the cell in grams
per amp-hr.

This definition of quality has units of amps/gram. The manufacturer's rated capacity of the cells under test should be used to determine the values of I , g , and the depth of discharge.

The individual cell failure qualities should also be calculated by Equation (A-2), by using 1.00 volt, compensated for IR , in place of the end-of-discharge voltage (E_{eod}).

During the testing of the cell groups, predictions should be made concerning their expected life. One method for making such predictions concerns parametric failures and is described elsewhere.⁽²⁷⁾ These predictions should be made by using the cells' initial quality and failure quality calculated with Equation (A-2).

All parametric failures, actual cell failures and the cells remaining at the conclusion of the test should be subjected to the failure analysis procedure listed in Table VIII of this report. The purpose of the failure analysis procedure is to determine whether the failure mechanisms are the same at all stress levels. One requirement for a valid accelerated life test is that the failure mechanism is the same at all stress levels.

Also after the tests have been completed, acceleration factors should be determined for each group based on the normal stress of Group 1, Table XVIII. The presently recommended method for determining the acceleration factors is described in this report in the section entitled "Verification Tests, Test Results". The student-T test is recommended to calculate confidence levels for the accelerated test procedure recommended in Table XVIII.

The experiment just described is the recommended test procedure for a typical near-earth orbital profile. If for some reason the cells, equipment, or

monies were not available to run this experiment, a minimal experiment would be to test Groups 1, 6, 7, 8, 9, and 10 with five cells instead of eight. This minimal experiment would provide only the minimum amount of statistical information involving two extrapolations and would not provide the electrochemist with the type of information he would like from such an experiment as was recommended. This minimal experiment would provide testing at the most stressful conditions (Group 10) and a means to relate this information back to the normal or operational test conditions (Group 1).

With the above information and the cited references, sufficient detail is believed to be available to permit a skilled technician to carry out the recommendations.